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Selenium Removal from Ground Water Using Activated Alumina

James M. Montgomery, Inc.
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16. ABSTRACT

Laboratory studies were performed to determine optimum conditions for using activated alumina to remove selenium from drinking water supplies. Column tests showed that the capacity of alumina for Se IV decreased as influent pH increased. Best removal of Se IV occurred at pH 5 where 1200 bed volumes of water, with influent concentration of 0.2 mg/L, were treated before breakthrough (Se conc. >0.01 mg/L) occurred. Optimum regenerant was 1.5 lbs/ft^3 of 0.5% NaOH at 1/2 gpm/ft^2 upflow and 0.7 lb/ft^3 of 0.25% H_2SO_4 at 1 gpm/ft^2 downflow. The capacity of alumina for Se VI decreased as either pH or sulfate concentration increased. Removal costs would be three to four times higher if Se VI is the predominant form of selenium present in water supply.

Tests showed that the flourometric technique can be used to determine Se IV concentrations. Atomic Absorption Spectroscopy remains the best method for total selenium and Se VI plus organic selenium concentratiions can be determined by difference.

Information from this project should be useful to research and design engineers, and state personnel concerned with the removal of selenium from ground water.

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SELENIUM REMOVAL FROM GROUND WATER USING ACTIVATED ALUMINA

BY

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Contract No. 68-03-1515

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

This report addresses the feasibility of removing selenium from drinking water supplies using activated alumina. This information is helpful to determining operating parameters for the activated alumina process, which can also remove arsenic and fluoride from drinking water supplies.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

ABSTRACT

Selenium is a contaminant found in trace quantities in some ground- and surface-waters in the United States. Currently, the National Drinking Water Regulations limit total selenium to .01 mg/l. Even though the health affects of selenium in "trace" amounts are still highly debatable, it is prudent to explore the technology of removing selenium from drinking water.

Two species of inorganic selenium, with valence states of +4 and +6, are typically found in selenium-contaminated waters. Se(IV) and Se(VI) act very different, chemically. Se(IV) occurs as $HSeO_3^-$ in the pH range of 2.7 to 8.5. Se(VI) occurs as $SeO_4^=$ above pH 1.7. The valence of either of these species is thought to be determined by the oxidation-reduction potential of a water at a certain pH. Knowing the oxidizing state of a water, one can predict whether Se(IV) or Se(VI) should be present.

Historically, only the total selenium present in a sample has been able to be determined by atomic adsorption spectroscopy. With the incorporation of a fluorometric technique to determine the Se(IV) in a sample, this study was able to differentiate between the two species of selenium.

Initial batch studies indicated that Se(IV) was preferentially adsorbed over Se(VI) in side-by-side tests. The isotherm capacity of activated alumina for Se(IV) was roughly three times the capacity of Se(VI). Other studies indicated that while bicarbonate mildly interfered with Se(IV) removal, both bicarbonate and sulfate heavily interfered with Se(VI) adsorption.

Initial column studies with a three-inch deep bed helped delimit the amounts of NaOH and H_2SO_4 to be used during regeneration of Se(IV)-saturated alumina. Other items addressed in the three-inch column studies included how varied concentrations

of NaOH and H_2SO_4 affected regeneration capabilities and how the varied concentrations affected alumina degradation.

Deeper (9-inch) column studies showed that capacities for Se(IV) decreased with increasing influent water pH. pH 5 showed the highest capacity for Se(IV) adsorption. The kinetics of regeneration were the most important factors in determining the capacity of activated alumina for Se(IV), with pore diffusion seeming to be the rate-limiting step. Slow 0.5% NaOH flow rates (0.5 gpm/ft^2 or less) are necessary to effectively recover a high percentage of Se(IV) removed during a previous treatment run. The following regeneration steps are recommended for Se(IV) removal:

1.5 lb/ft^3 of 0.5% NaOH at 1/2 gpm/ft^2, upflow
5 bed volumes of water at 1-2 gpm/ft^2, downflow
0.7 lb/ft^3 of 0.25% H_2SO_4 or HCl at 1 gpm/ft^2, downflow
5 bed volumes of water rinse at 1-2 gpm/ft^2, downflow

The following bed volumes of treated water can be expected to be produced with a Se(IV) influent concentration up to 200 ppb:

pH 5 -	1200	bed volumes
pH 6 -	900	bed volumes
pH 7 -	500	bed volumes

Selenium (VI) is much more poorly adsorbed than Se(IV). It is suspected that this low adsorption is due to Se(VI)'s higher solubility with the oxides of alumina. Because of this poorer adsorption, NaOH regeneration amounts and flow rates are not as important in recovering Se(VI) removed during a treatment run. Because $SO_4^=$ heavily interferes with Se(VI) adsorption by activated alumina, only HCl can be used as the acid rinse during regeneration.

Capacities of activated alumina for Se(VI) are shown below at the following pH's for an influent concentration of 50 ppb:

pH 5 - 100 bed volumes
pH 6 - 70 bed volumes
pH 7 - 35 bed volumes

These capacities are based on a $SO_4^{=}$ concentration of 100 ppm. The following capacities were developed for Se(VI) at different sulfate concentrations at pH 6:

$SO_4^{=}$ = 5 ppm - 450 bed volumes
$SO_4^{=}$ = 50 ppm - 150 bed volumes
$SO_4^{=}$ = 100 ppm - 70 bed volumes
$SO_4^{=}$ = 500 ppm - 15 bed volumes

Variations in capacity for Se(VI) with different amounts of bicarbonate were not as great.

Preliminary cost estimates were done to predict costs of treatment for either a Se(IV) or a Se(VI) contaminated supply. Costs are as follows:

Se(IV) - $ 75/acre-foot
Se(VI) - $255/acre-foot

If a mixture of the two species is present, Se(VI) concentrations will determine the cost of treatment.

This report was submitted in fulfillment of Contract No. 68-03-1515 by James M. Montgomery, Consulting Engineers, Inc. under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period April 1, 1979 to March 21, 1980, and work was completed as of April 21, 1980.

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SECTION 1

INTRODUCTION

BACKGROUND

Selenium is a controversial contaminant found in trace quantities in some ground waters and surface waters in the United States. Selenium is known to be an essential nutrient in minute quantities, but prolonged exposure to higher concentrations has been known to bring about respiratory disease and death. Investigators have reported that selenium is a carcinogen and others have claimed that it has anti-carcinogenic effects.

The current Federal limit for selenium in drinking water is 0.01 mg/l. While toxicological research continues looking into the health effects of selenium, it is prudent to investigate concurrently the technology for removing selenium from water. Little accurate data on selenium in drinking water is currently available. As analytical techniques for selenium become more accurate, more systems may be affected.

SELENIUM

Unfortunately, data on the presence of selenium in drinking water supplies are limited. The data that are available suggests that one would rarely find surface waters containing appreciable (>0.01 mg/l) amounts of the element[1]. Its presence in higher concentrations (>0.050 mg/l) appears to be limited to ground waters. Up to 0.48 mg/l has been reportedly found in a well in Nebraska[2]. Other known wells with relatively high amounts of selenium have been found in Southern and Central California, Colorado, South Dakota, and Wyoming.

Inorganic selenium occurs in valence states of +4 and +6 in aqueous solutions. It is assumed that their presence in natural ground water is due to seleniferous formations within the aquifer. Selenium (IV) occurs as the anion $HSeO_3^-$ in the range of pH's from 2.7 to 8.5. Selenium (VI) occurs as the anion $SeO_4^=$ above pH 1.7. The speciation of each oxidation state is given in more detail in the concentration -pH diagrams in Figure 1.

Selenate (Se(VI)) in the form of selenic acid (H_2SeO_4) is comparable in strength to sulfuric acid. In solubility, most salts of selenic acid are similar to the sulfates of the same metals. Selenite (Se(IV)) in the form of selenious acid (H_2SeO_3) is a weak acid. Most selenite salts are less soluble than the corresponding selenates.

The behavior of selenium in various environments may be best determined by an examination of the reduction-oxidation (redox) potentials for its various oxidation states as a function of pH. The E_h - pH diagram for selenium, shown in Figure 2, can be explained as follows: Each line on the diagram represents equilibrium between the oxidized form written above the line and the reduced form written below it. The space between two lines is the stability field of the ion or molecule shown on the upper side of the lower line and the lower side of the upper line.[3] The dashed lines represent the stability limits of H_2O. The shaded area shows the normal range of waters from pH 6.0 to 8.5, which is the region of interest in this discussion.

The upper portion of the shaded area represents a highly oxidized situation. Well aerated surface waters having a high oxidation potential would fall in this region. So alkaline surface waters with selenium present should show a great majority of Se(VI). Any Se^o could be oxidized to $HSeO_3^-$ in alkaline or mildly acidic conditions or the $HSeO_3^-$, in turn, could oxidize to $SeO_4^=$.

Selenite could be rapidly reduced to elemental selenium by mild reducing agents such as SO_2. Selenate has been found to be more stable and there is less probability that selenate could be reduced to selenite under mild reducing conditions, but the diagram shows that selenate is also unstable in a reducing environment over the long term.

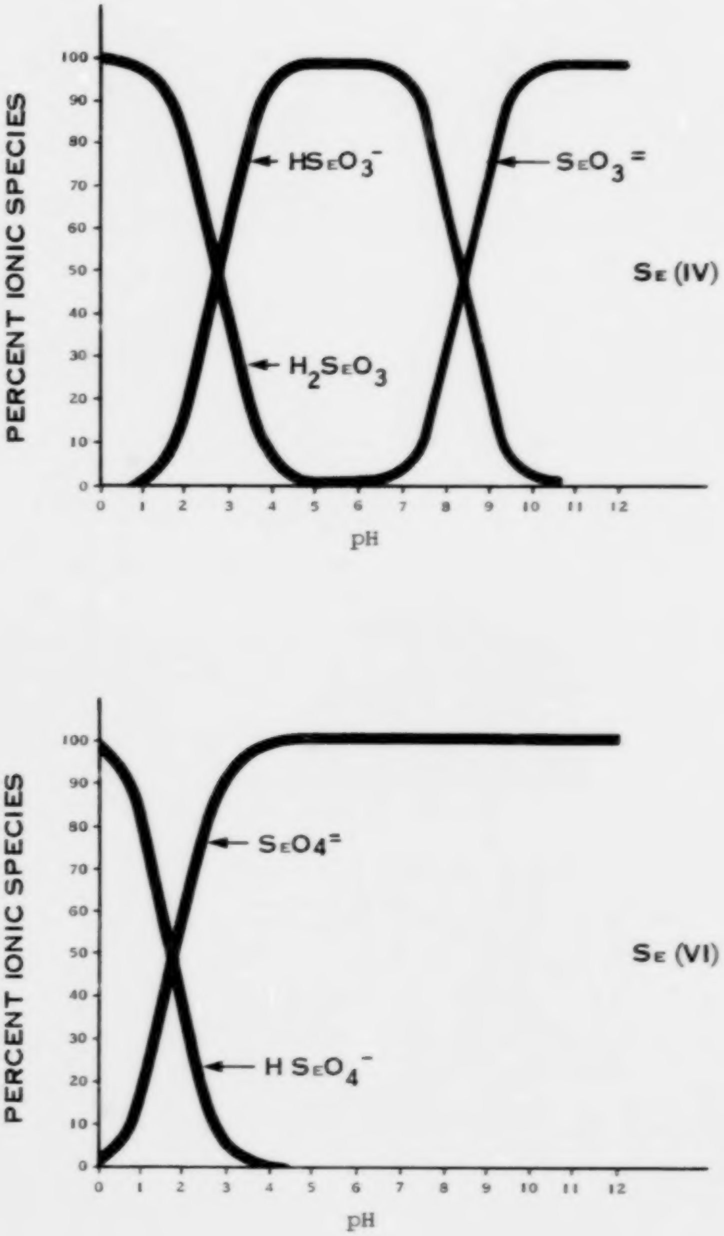
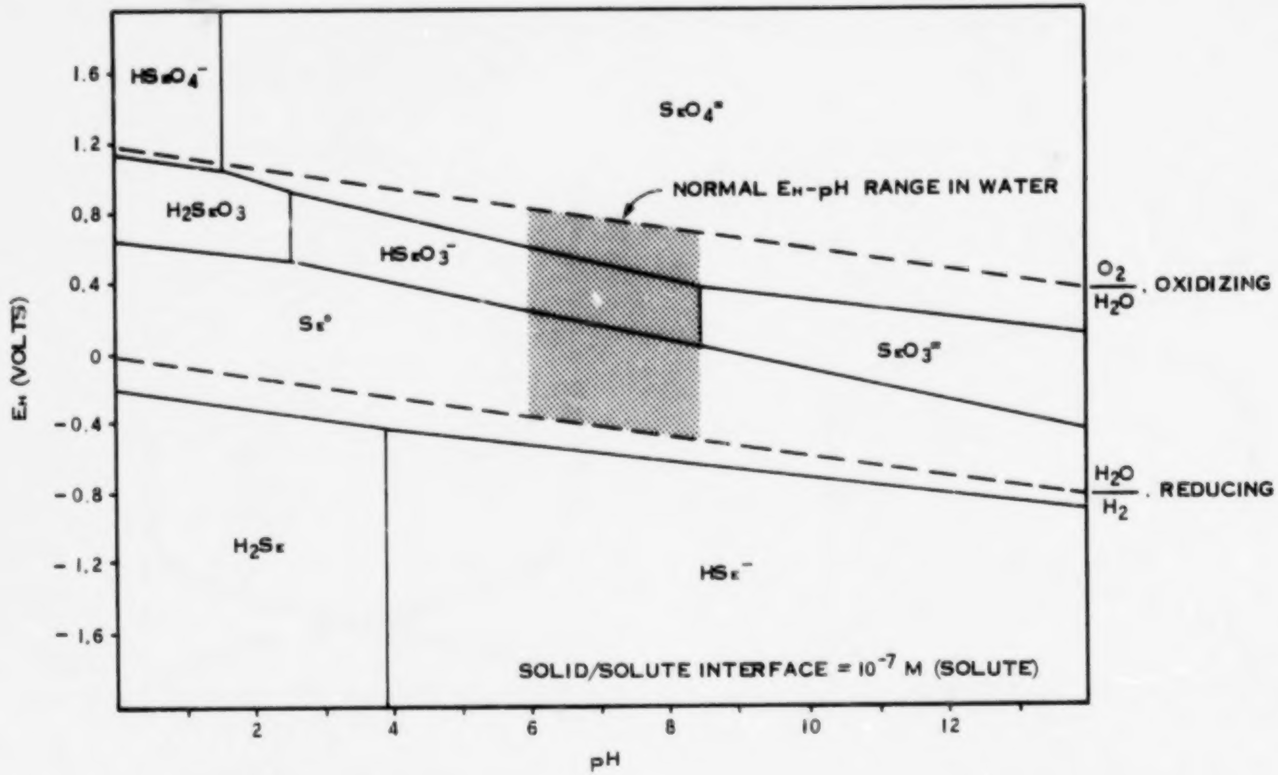


Figure 1. Concentration -pH diagrams for inorganic selenium species.



CONSTANTS PER TABLE I-I

Figure 2. Eh - pH diagram for selenium.

TABLE 1

CONSTANTS USED TO CONSTRUCT E_h-pH DIAGRAM

Half-Reaction	Potential (Volts)	Source of of Constant
$SeO_4^{=} + 4H^+ + 2e^- = H_2SeO_3 + H_2O$	1.15	1
$SeO_4^{=} + H_2O + 2e^- = SeO_3^- + 2OH^-$	0.05	1
$H_2SeO_3 + 4H^+ + 4e^- = Se + 3\,H_2O$	0.74	1
$SeO_3^{=} + 3\,H_2O + 4e^- = Se + 6OH^-$	-0.37	5
$Se + 2H^+ + 2e^- = H_2\,Se\,(aq)$	-0.40	1
$Se + 2e^- = Se^-$	-0.92	1

Acid-Base Reaction	pK	Source of Constant
$H_2\,SeO_3 = H^+ + HSeO_3^-$	2.75	2
$H\,SeO_3^- = H^+ + SeO_3^{=}$	8.50	2
$H_2SeO_4 = H^+ + H\,SeO_4^-$	-3	4
$H\,SeO_4^- = H^+ + SeO_4^{=}$	1.66	2
$H_2Se(aq) = H^+ + HSe^-$	3.89	2
$HSe^- = H^+ + Se^{=}$	15.0	2,3

1. Latimer, W., "Oxidation Potentials" 2nd Ed., Prentice-Hall, N.Y., 1952.

2. Baes, C.F. and Mesmer, R.E., The Hydrolysis of Cations, Wiley-Interscience, N.Y., 1976.

3. Sillen, L.G. and Martell, A.E., Stability Constants of Metal-Ion Complexes, Metcalf and Cooper, Ltd., London, 1964.

4. Langes' Handbook of Chemistry, 12th Ed., Editor-J. Dean, McGraw Hill CO., N.Y. 1979.

In waters with low levels of oxygen, the oxidation potential is reduced. Depending on the actual oxidation potential of the water, a combination of Se(IV), Se(VI), and Se^o could be present. A ground water would be expected to offer conditions where selenium could be present as a mixture of Se(IV) and Se(VI).

There is ambiguity concerning the redox potential between Se^o and H_2Se. It may be possible in a very reduced condition that selenium as HSe^- could be formed in natural waters. However, the occurrence of free selenide (H_2Se, HSe^-, and $Se^=$) in ground waters is unlikely due to its rapid formation of precipitates of iron. Evidence has been presented to suggest that when selenites react with ferric chloride, a very insoluble precipitate that approximates the composition of basic ferric selenite, ($Fe_2(OH)_4Se0_3$) is also formed.[3] This will also happen with aluminum to a lesser extent.

Based on the information presented, the presence of either Se(VI) or Se(IV) in a water depends on many factors concerning the chemistry of the particular water of interest. From the E_h-pH diagram, a poorly aerated ground water could have a varied combination of Se(IV) and Se(VI). Because of Se(IV)'s lowered solubility, any iron present in a water would tend to form insoluble precipitates with it. Elemental selenium presents no problem in aqueous considerations. Therefore, Se(VI) would appear to be the most common species present in a generalized groundwater condition.

Organic selenium occurs in natural aqueous solutions as (CH_2) Se, (CH_3) Se_2, and other forms by the means of microbiological assimilation and degradation. Although measurements are not available, organic selenium compounds are not thought to be a large component of total selenium in groundwater. Most of the knowledge about organic selenium has been derived from work involving synthetic organic selenium compounds. From this work, it is known that essentially all of the synthesized compounds contain selenium in the -2 oxidation state and that these compounds tend to oxidize and form elemental selenium.[4]

PRIOR RESEARCH

In an effort to provide information explaining how the drinking water requirement for selenium could be most effectively met, the Water Supply Research Division of EPA conducted a research program consisting of jar test studies and bench tests. Ferric sulfate coagulation, alum coagulation, and lime softening were studied for Se(IV) removal. Ferric sulfate removed 85% of Se(IV) at a pH of 5.5 or less with an initial Se(IV) concentration of 0.03 mg/l. Lime softening removed 45% with a well water and Se(IV) concentration of 0.03 mg/l. Alum coagulation was unsuccessful, removing only 20% at best.[2,5] Coagulation by ferric sulfate, ferrous sulfate, alum, and lime softening were unsuccessful for Se(VI), 10% removal being the best. However, ion exchange and reverse osmosis were found to both remove greater than 95% of either Se(IV) or Se(VI) from drinking water.[2,5]

Because coagulation and lime softening were not always effective or applicable to small water systems, and because of the great costs associated with demineralization by ion exchange or reverse osmosis processes, the EPA initiated investigations of the use of activated alumina for removal of selenium. Activated alumina has been successfully used in studies to remove phosphate, fluoride, silica, and arsenic from drinking water and phosphates from wastewaters.[6,7,8,9,10,11,12] It is currently being used in two full-scale fluoride removal facilities.[13] Alumina is about one-tenth the cost of most ion exchange resins and researchers have reported that it doesn't remove sulfate, chlorides, and other anions that would compete with selenium removal by anion exchange treatment.[2]

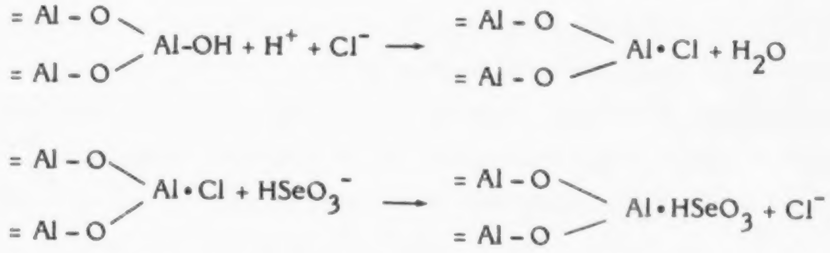
ACTIVATED ALUMINA

Activated alumina is produced by thermal treatment of hydrated alumina, the alumina being extracted from bauxite ore. It has a great affinity for water and is generally used as a dessicant for drying gases and liquids. Activated alumina is produced mainly by the Aluminum Company of America (ALCOA) and the Reynolds Aluminum Company. The activated alumina produced by ALCOA is available in several grades: F-1, F-5, and F-6. Type F-6 is a chromatographic alumina and costs about eight times as much as type F-1. Type F-5 is considered a specialty product and is also more costly than F-1. Type F-1 is the general grade of activated alumina available and is practically 100 percent alpha alumina. It is the most inert of all the alumina oxides. F-1 is the grade used in these studies and some of the technical aspects are shown below:

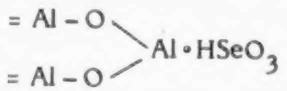
Chemical constituents:	Al_2O_3		92.2%
	Na_2O		0.9%
	Fe_2O_3		0.08%
	Loss on ignition		6.5%
Physical Properties:	Surface Area	=	250 m^2/g
	Loose Density	=	52 lb/ft^3
	Packed Density	=	55 lb/ft^3
	Specific Gravity	=	3.3
	Graded Mesh Ranges	=	8-10, 14-28, 28-48, 48-100

Adsorbents are defined as natural or synthetic materials of micro-cystalline structure, whose internal pore surfaces are accessible for selective combination of solid and solute. Usually the attractive forces are weaker and less specific than those of chemical bonds. Its selective action is most pronounced in a monomolecular layer next to the solid surface, but at times selectivity may persist to a height of three or four molecules.[14] Adsorption capacity of a solid for a solute tends to increase with the fluid-phase concentration of the solute.

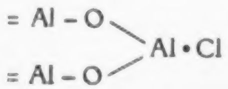
As discussed by Kubli, adsorption of inorganic salts on alumina is due to hydrolytic adsorption associated with aluminum and hydrogen ion exchange. If alumina is treated with an aqueous acid solution, the Al_2O_3 will be charged to a hydroxyl-bearing cation capable of binding the anions of various salts as water-insoluble salts. If, for example, the acid is HCl, hydrogen ions from the acid react with some of the attached hydroxide ions of the solid alumina to yield water molecules, which remain attached to the alumina. The network of aluminum and water molecules then acquires a positive charge. The anions of the acid become included in the solid as counter-ions, and electroneutrality occurs. These counter-ions, since they are not built into the network, will readily exchange and these ions are expected to be exchanged when the solid comes in contact with a less soluble anion. If Se(IV) is in solution as $HSeO_3^-$, $HSeO_3^-$ will readily replace the chloride ion (Cl^-) provided that the solubility of the chloride complex is greater than the selenite complex. The mechanism can be explained by the following diagrams:



provided that the solubility of



is lower than that of



Since activated alumina is an amphoteric substance, it will adsorb cations at pH's above its isoelectric point and anions in more acidic environments. This phenomona can be explained by the net surface charge on the alumina. The isoelectric point is defined as the particular pH where the net surface charge is zero. For type F-1 alumina, this point is at pH 9.2.

A phenomena called secondary adsorption is known to exist with alumina. This occurs when cations bond to anions and then other anions adjacently link onto the cations and vice versa. This effects a chain of ions. Secondary adsorption occurs as (1) joint adsorption of anions with multivalent cations and (2) joint adsorption of cations with multivalent anions. There appears to be no adsorption with univalent anions and univalent cations[2]. This may explain why the hardness ions, calcium and magnesium, seem to be partially removed during a removal run at pH's in the range of 6-8.

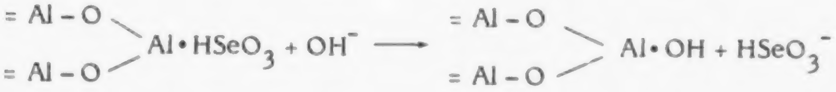
Kubli developed an anion selectivity series for activated alumina based on his work with a few anions of interest. They are, in order of decreasing preference:

OH^-, PO_4^{3-}, F^-, SO_4^{2-}, Cl^-, NO_3^-, ClO_4^-

It is presumed that Kubli did his work at a normal operating pH in the range of 5 to 8 and thus the anion being removed instead of PO_4^{3-} would be $H_2PO_4^-$. Part of the research discussed in this report involves the development of a broadened series which includes other trace inorganics of interest, namely Se(IV), Se(VI), As(III), As(V) and another anion found in large amounts in every water supply, HCO_3^-.

Kubli suggested that elution of the alumina after adsorption of the species of interest had taken place could be done by any of three mechanisms:

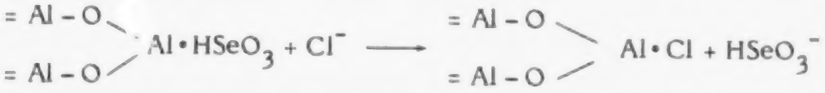
(1) Alkali (OH^-) elution, where the heavily favored hydroxide ion displaces all other species in or on the sites,



$$\begin{matrix} =Al-O \\ =Al-O \end{matrix} \Big> Al \cdot HSeO_3 + OH^- \longrightarrow \begin{matrix} =Al-O \\ =Al-O \end{matrix} \Big> Al \cdot OH + HSeO_3^-$$

(2) by contact with other anions which form less soluble basic aluminum salts,

(3) by contact with higher concentrations of the original anion bound to the alumina (in this case Cl^-).



$$\begin{matrix} =Al-O \\ =Al-O \end{matrix} \Big> Al \cdot HSeO_3 + Cl^- \longrightarrow \begin{matrix} =Al-O \\ =Al-O \end{matrix} \Big> Al \cdot Cl + HSeO_3^-$$

The most feasible option would seem to be elution with a concentrated amount of sodium hydroxide. Ames[8] tried NaOH and Na_2CO_3 as regenerants and NaOH was found to be more efficient. Since optimum removals of anions should occur at a pH less than 9.2, the now basic alumina must be eluted with an acid to lower the pH. Preferably, this acid's anion will not effectively complete with the species to be adsorbed for sites on or in the alumina. Based on Kublis's results, perchloric, nitric, hydrochloric, and sulfuric acids would be the preferred neutralizers, in decreasing order of preference. Unfortunately, the relative costs of these acids are in the reverse order, perchloric being most costly and sulfuric being the cheapest.

Various investigators have completed studies to determine activated alumina's ability to remove the anions fluoride, silica, and arsenic.[6,7,10,12] In batch tests, Choi and Chen[19] determined that to achieve a final fluoride level of less than 1 mg/l requires an initial fluoride concentration lower than 40 mg/l with an adsorbent dosage of 25 g/l. They found that the presence of other chemical species does not seriously interfere with fluoride removal by activated alumina. pH was found to be the most critical factor in determining the fluoride removal efficiency. The optimum pH was around 6.

Gupta and Chen[6] investigated arsenic removal by activated alumina in the batch mode. As before, pH played a major role in determining the capacity for arsenic removal. Good removals were achieved in the pH range of 4 to 7. However, arsenic is present in two valence states in water, +3 and +5. At pH 6.5, As(V) is present as $H_2AsO_4^-$, while at pH 9, As(III) is present as H_3As0_3. Arsenic (V) removals were on the order of 10-20 times greater than were arsenic (III) removals under the same testing conditions. Another difference from fluoride is that the presence of other chemical species in the matrix reduced by as much as 80 percent the amount of arsenic removed. As(V) adsorption was affected much more by chemical composition than was As(III). Oxidation of As(III) to As(V) is necessary to achieve effective arsenic removal and chlorine has been successfully used to accomplish this.

Clifford and Matson[12] determined that the optimum pH range for silica removal by activated alumina is 8.0-8-.5. They believe that the ion $Si(OH)_30^-$ is being removed and that this removal is optimal near the pK for ionization of $Si(OH)_4$, which is 9.5. Varied levels of sulfate were found to have little effect on the capacity of activated alumina for silica. However, the presence of fluoride in the water greatly affected the capacity for silica.

There has been some work using continuous flow activated alumina columns as a means of determining the removal capacity of the element of interest. Rubel[13] has reported the optimum operating conditions for a full-scale fluoride removal facility. He used 5 feet of alumina in a six-inch diameter column. After a treatment run was finished, the following regeneration procedure was as follows:

Backwash: 2.5 bed volumes of treated water @ 9 gpm/ft^2, upflow
Regeneration: 2.5 bed volumes of 1% NaOH @ 2½ gpm/ft^2, downflow
Intermediate Rinse: 4 bed volumes of treated water @ 5 gpm/ft^2, upflow
Neutralization: 3 bed volumes of 0.5% H_2SO_4 @ 2½ gpm/ft^2, downflow

Neutralization is done by continually adjusting the pH of the raw water with H_2SO_4 until the pH of the treated water reaches that of the raw water (pH - 5.5). The above mentioned step is the equivalent and is used to determine the actual amount of H_2SO_4 used to neutralize the bed.

Treatment: Usable water is produced after the pH of the treated water reaches 9.0. Here, significant fluoride removal will start to occur.

With this treatment, he is able to produce 1400 bed volumes of treated water with an average F^- concentration of 0.8 mg/l, from an initial concentration of F^- of 5.0 mg/l.

In 1970, Bellack[9] did some testing in the laboratory to see if activated alumina could remove arsenic from water supplies. His brief work suggested the following procedure:

Backwash: 15 bed volumes of tap water @ 9 gpm/ft^3, upflow
Regeneration: 4 bed volumes of 1% NaOH @ 1 gpm/ft^2, downflow
Intermediate Rinse: 8 bed volumes of distilled water @ 1 gpm/ft^2, downflow
Neutralization: 4 bed volumes of 0.1 N H_2SO_4 @ 1 gpm/ft^2, downflow
Final Rinse: 4 bed volumes of distilled water @ 1 gpm/ft^2, downflow
Treatment: Raw water at 2 gpm/ft^2, downflow

The final rinse is necessary to remove the excess 0.1 N H_2SO_4 from the bed. This was not needed in Rubel's facility because the raw water's pH was adjusted with H_2SO_4 to perform the neutralization step and the pH was stepwise increased as the pH of the treated water dropped. Bellack stated that with an initial concentration of 0.10 mg/l total arsenic, approximately 900 bed volumes of water with an arsenic concentration less than 0.01 mg/l can be produced. However, he failed to mention whether arsenic in the +3 or +5 valence state was present. He probably did not note the difference in the two species and made no effort to determine the speciation.

Ames[8] used fairly large (5.1 cm D x 49 cm H) columns to determine the removal of phosphates from wastewater using activated alumina. He was able to remove approximately 90% of all phosphates applied for 400 bed volumes. He concluded that varied amounts of sulfate present in wastewater had little effect on phosphate removal. pH was not selectively controlled in his experiments, but operating above pH 8.0 led to precipitation and calcium carbonate fouling of the alumina.

He prescribed the following regeneration:

8 bed volumes of 1 M NaOH @ 3 gpm/ft^2
20 bed volumes of washwater @ 3 gpm/ft^2

No acid rinse was used after a caustic elution due to his apparent lack of concern about the operating pH of the treatment cycle. It was also noted that from 1% to 5% of the column bed was lost per elution, making it necessary to replace the activated alumina often.

PROJECT APPROACH

The approach of this project to determine the feasibility of removing selenium from drinking water using activated alumina was developed so that each progressive phase contributed to the following phase. The project was divided into three phases: I. Analytical Techniques, II. Batch Isotherm Tests, and III. Bench Scale Column Studies. Straightforward techniques for the analysis of Se(IV), Se(VI), and organic selenium in water and an important prerequisite as they helped facilitate full concentration on the selenium removal process itself. Adsorption isotherms were used to determine the rough parameters for column studies. The column tests helped to determine optimum regeneration techniques, selenium breakthrough capacities, and interferences by other ions.

The column studies should provide relevant information to efficiently test this process at the pilot scale. This should be the next phase in studying the activated alumina process for seleniumn removal. A pilot plant study can produce the engineering data required to determine the feasibility of using activated alumina to remove selium from drinking water.

It should be noted that the columns studies contain quite a bit of information. Initial testing done with three-inch columns of alumina may not provide the reader with a good understanding of the actual capacity information that was developed with the nine-inch columns. However, the short column runs did provide us with enough information to narrow down operating parameters with regards to regenerative processes.

To develop a clear understanding of the sequential development of the experimental design, it is suggested that the "Summary of Results", Table 6, be reviewed prior to reading the discussion of the results of each successive run. The results of all the tests performed during this work are presented in this report. For a rapid review of the data, the reader may wish to skim through the section discussing the three-inch column work.

SECTION 2
CONCLUSIONS

ANALYSIS

The Atomic Absorption Spectrophotometer (AAS) can be used to determine the total selenium present in a sample. The method is quick, sensitive, and produces reliable results. Selenium (IV) can be differentiated from other forms of selenium by using a fluorometric technique. This method requires a very small sample, 10 ml, but its limitation is the amount of time required to complete the analysis. Depending on the amount of glassware available to the analyst, 10 samples can be analyzed in approximately 6 hours. Although its reliability has not been proven over time, the analysis was found to be reproducible in our experiments.

Methods evaluated for the detection of organic selenium compounds proved to be complex and subject to interferences. Although the literature shows that these techniques can be feasible in a research environment, they were determined unsuitable for routine monitoring at concentrations less than 100 µg/l. Samples to be analyzed for different species of selenium were determined as: (1) total selenium (by AAS), (2) selenium (IV) (by fluorometry), and (3) selenium (VI) and organic selenium (by difference).

BATCH STUDIES

As part of the overall bench scale testing program, batch tests were necessary to determine the effect of various parameters on the adsorption of selenium by activated alumina.

Preparation (Regeneration)

Fresh activated alumina must be initially prepared for selenium adsorption, the preparation being similar to proposed regeneration techniques to be used in column studies. Optimum finding, were:

- 1% NaOH rinse for 50 minutes
- 5-minute deionzed water rinse
- 0.05 N HCl rinse for 10 minutes (to be used when removing Se(VI)) or
- 0.05 N H_2SO_4 rinse for 10 minutes (to be used when removing Se(IV))
- 2 to 4 deionized water rinses for 5 minutes each

H_2SO_4 worked only slightly better than HCl in preparing the alumina for Se(IV) removal. HCl worked much better than H_2SO_4 in preparing the alumina for Se(VI) removal.

Kinetics

Sixty minutes contact time between the selenium stock solution (100 ppb) and the activated alumina (8.33 g/l) were necessary to ensure equilibrium had been reached. Tests showed that up to 95 percent of selenium (IV) could be removed in the first ten minutes of contact. Up to 80 percent removal of selenium (VI) was found in the first ten minutes of contact with activated alumina.

pH Effects

pH in the range of 3 to 7 did not affect Se(IV) removal. Removal efficiencies appear to have dropped off above pH 7. Results on Se(VI) were widely varied and showed no general trend with regards to pH. Since activated alumina is amphoteric, pH should have a large effect on both Se(IV) and Se(VI) removal. This was not seen in these tests. Work done by Ball[2] indicated that both Se(IV) and Se(VI) adsorption was enhanced at lower pH.

Mesh Sizes

Three different mesh sizes were tested as to their capability of quickly adsorbing selenium once in contact with activated alumina. The general rule of thumb is the smaller the mesh size, the more rapid the adsorption. This is true for both Se(IV) and Se(VI).

Interfering Ions

Of the anions tested, bicarbonate had the most pronounced effect on selenium (IV) adsorption. It reduced removals by approximately 10 percent. Chloride, nitrate, and sulfate only marginally interfered with selenium (IV) removal. Both sulfate and bicarbonate heavily interfered with selenium (VI) adsorption at concentrations greater than 100 mg/l. Greater than 60 percent reduction in the adsorptive capacity of activated alumina for Se(VI) was noticed with these two anions. Chloride and nitrate had no pronounced effect.

Three cations; sodium, magnesium, and calcium were evaluated for interferences. None of these ions in concentrations as high as 200 mg/l negatively effected adsorption of either selenium (IV) or (VI). Some enhancement of adsorption was noticed at high concentrations. This is thought to be due to secondary adsorption effects.

Selectivity Series

In equi-molar concentrations, a part of Kubli's preferred anion list for activated alumina was verified, with additional anions of arsenic and selenium tested. Results were (at pH 6.5):

$$OH^- > H_2PO_4^- > F^- > H_2AsO_4^- > HSeO_3^-$$

Because of poor detection limits, the following species that are less preferred than the above five anions could not be relatively listed. Based on column studies, they are listed in assumed order:

$$SO_4^= > SeO_4^= > HCO_3^- > Cl^- > NO_3^- > H_3AsO_3$$

Capacities of Activated Alumina

In side by side tests with Se(IV) and Se(VI), activated alumina exhibited a greater capacity for Se(IV) in matrices of deionized water and a synthetic well water. Activated alumina was found to have approximiately 3 times the capacity for Se(IV) than for Se(VI), based on a Freundlich isotherm model.

COLUMN STUDIES

Selenium (IV)

Using a synthetic well water modeled after a known ground water with high selenium concentrations and a 9-inch deep bed of activated alumina, the following capacities for Se(IV) were developed at a surface loading rate of 3 gpm/ft^2 (7.3 meters/hour):

pH 5 - 1,200 bed volumes $= 235 \frac{\text{mg Se(IV)}}{\text{liter of activated alumina}}$

pH 6 - 900 bed volumes = 175 mg/l

pH 7 - 500 bed volumes = 100 mg/l

The above breakthrough capacities (the amount of Se(IV) alumina will adsorb before the effluent concentration becomes greater than 0.01 mg/l) are based on an influent concentration of 200 ppb (=0.20 mg/l), with regeneration by 0.5% NaOH at a dose of 1.5 #NaOH/ft^3 bed (24 g/l) at a flow rate of 0.5 gpm/ft^2 (1.2 meters/hour). A slower regeneration rate may increase the above capacities. The effect of actual flow-through contact time between the NaOH and the activated alumina was the greatest of any parameters tested with regards to capacity. At 0.5 gpm/ft^2 NaOH flow rate, roughly 90% of the Se(IV) removed during the treatment run was recovered in the regeneration.

For lower influent concentrations of Se(IV), the actual capacity is assumed to be a linear function of the influent concentration. Therefore, an influent Se(IV) concentration of 50 ppb should produce a capacity of roughly 60 mg/l at pH 5.

Similarly, the capacities at pH 6 and pH 7 showed 45 mg/l and 25 mg/l, respectively. However, to reach an effluent concentration of less than 10 ppb, similar bed volumes of treated water will be produced regardless of the influent concentration up to 200 ppb.

Neutralization of the activated alumina after NaOH rinsing can be successfully accomplished with either H_2SO_4 or HCl. The following regeneration scheme was determined for this study:

5 bed volumes 0.5% NaOH @ 0.5 gpm/ft^2, up
5 bed volumes D.I. water @ 1 gpm/ft^2, up
6 bed volumes 0.05 N H_2SO_4 or 0.05 N HCl @ 1 gpm/ft^2, up
5 bed volumes D.I. water @ 1 gpm/ft^2, up

All the regeneration steps were done in the upflow mode to facilitate rapid testing. Upflow regeneration by NaOH is recommended, but the remaining steps should be done downflow in a full-scale removal facility.

The NaOH and H_2SO_4 (or HCl) tend to dissolve the activated alumina and how fast it degrades is dependent on acid or base concentration and flow rate. Higher concentrations will dissolve slightly more alumina and slower flow rates will dissolve more alumina than more rapid regeneration. The above-mentioned regeneration steps dissolved, on the average, the following percentages of a nine-inch bed (by weight):

NaOH - 0.9% per regeneration
H_2SO_4 (or HCL) - 0.08% per regeneration

Annual media replacement will depend on how often regeneration is done. pH adjustment for removal of Se(IV) can be done with either H_2SO_4 or HCl. HCl was used for these tests.

Selenium (VI)

Using a similar synthesized water as with Se(IV) the following capacities for Se(VI) with a nine-inch bed of activated alumina were developed at a surface loading rate of 3 gpm/ft^2:

pH 5 - 100 bed volumes = 4.5 mg Se(VI) liter of activated alumina
pH 6 - 70 bed volumes = 3.2 mg/l
pH 7 - 35 bed volumes = 1.6 mg/l

The above breakthrough capacities are based on an influent concentration of 50 ppb Se(VI) with regeneration by 0.5% NaOH at a dose of 1.5 #NaOH/ft^3 bed at a flow rate of 2 gpm/ft^2. This capacity is one-twelfth the capacity for Se(IV) based on equivalent influent concentrations of Se(IV) and Se(VI).

Rate of regeneration was not as critical as with Se(IV) and a smaller NaOH dose could be used to achieve similar breakthrough capacities. This is due to Se(VI)'s relatively low position in activated alumina's selectivity series. Regeneration is much less dependent on diffusion-controlled kinetics.

The other regeneration steps were the same as with Se(IV), except only HCl can be used to neutralize the bed. Sulfate from an H_2SO_4 rinse heavily interferes with alumina's capacity for Se(VI).

Due to the noticeable difference in acid rinses, tests were done to determine the effect of varied concentrations of two interfering anions, $SO_4^=$ and HCO_3^-. Decreased amounts of sulfate in the water greatly increased the capacity of activated alumina for Se(VI). The following list shows these capacities at pH 6:

SO_4^{-2}(ppm)	Se(VI) capacity (mg/l)	Bed Volumes
500	0.7	15
100	3.2	70
50	7.0	150
5	21.0	450

Similar tests with bicarbonate alkalinity interference did not show as great a difference at pH 6, as listed below:

Alkalinity (ppm as $CaCO_3$)	Se(VI) capacity (mg/l)	Bed Volumes
500	1.5	33
100	3.2	70
50	4.0	90
5	5.5	125

The above capacities are for an influent Se(VI) concentration of 50 ppb. Sulfate tests were done with approximately 100 ppm alkalinity, while the alkalinity tests were done with a sulfate concentration of about 100 ppm.

pH adjustment must be done with HCl. H_2SO_4 addition would increase the sulfate level and interfere with Se(VI) removal.

COSTS

Preliminary cost estimates were developed based on the capacities and regeneration techniques developed during this study. Annual costs were developed for amortized capital costs over 20 years, which included equipment, piping, instrumentation, a small building, clearwell, activated alumina, and land. Annual operation and maintenance costs included chemicals, labor, media replacement, and electricity.

These costs were developed to treat a water supply of 1 MGD with similar quality to that tested in this study contaminated solely with either a Se(IV) or Se(VI) concentration of 0.10 mg/l (100 ppb). Costs are:

Se(IV) - 23¢/1000 gal = $ 75/acre-foot
Se(VI) - 78¢/1000 gal = $255/acre-foot

Costs for removal of Se(VI) appear to be prohibitive. Since there is no cheap and relatively safe way to reduce Se(VI) to Se(IV), the feasibility of treating a water supply to remove selenium to less than 0.01 mg/l (10 ppb) depends on the amount of Se(VI) present in the water.

Based on an evaluation of the equilibrium between the various oxidation states of selenium in water, Se(VI) is expected to be predominately in well-aerated waters. In waters with lower oxidation potentials, Se(IV) and Se(VI) would be present in varied amounts.

SECTION 3
RECOMMENDATIONS

Because the speciation of inorganic selenium in water determines the cost of removal, a survey of known selenium-contaminated ground water sources should be analyzed to determine the relative amounts of Se(IV) and Se(VI). Since few actual determinations of the speciation in ground water have been done, this would be helpful in assessing conditions.

The inability to determine the presence of organic selenium compounds in a water sample in amounts less than 100 ppb makes this problem of great concern. Efforts should be made to modify the techniques described in Section 4 or to develop a new method for detecting organoselenium compounds in the microgram-per-liter range, since its presence may hinder the removal process by activated alumina. Perhaps a GC/MS sparge and trap method could be used.

NaOH regeneration of Se(IV)-saturated, activated alumina should be optimized to establish actual flow-through contact time and dose of NaOH required. Work done in this study indicates that a longer contact time may increase the amount of Se(IV) displaced during regeneration. It is possible that smaller amounts of NaOH could be used than were used on a day-to-day basis during these studies. Because Se(VI) is removed much less than Se(IV) in removal runs, the regeneration did not play as large a role in determining its capacity on activated alumina.

Based on Kubli's assumptions, chloride (Cl^-) might be able to regenerate selenium-saturated activated alumina if present in high enough concentrations. We recommend that some testing be done to evaluate this claim, since the cost of NaCl is much cheaper than that of NaOH and/or HCl. Sulfate, in the form of Na_2SO_4, might be a better regenerant for Se(IV) than chloride, but its interference with Se(VI) adsorption makes it unfeasible.

Pilot-scale testing is necessary to successfully model a full-scale selenium removal facility. Since a number of factors (SO_4^{2-}, HCO_3^-, pH) affect the removal of Se(IV) and Se(VI), the general water quality of the source should be evaluated. Sparse data gathered from Ramona Municipal Water District in a series of well samples showed that selenium concentrations varied quite a bit. Continuous pumping should be done to verify the steady-state concentrations of Se(IV) and Se(VI) before designing pilot-scale tests to evaluate activated alumina's feasibility.

Actual pilot testing should be done to refine the techniques developed in this study. Removal capacities, regeneration techniques and hydraulic characteristics should all be carefully studied to allow for an economic design of a full-scale removal facility, should it be deemed feasible. Deeper columns may produce more bed volumes of treated water than is shown in the 9-inch column used in this study. Determination of the optimum method for neutralizing the alumina with acid after the caustic rinse should be looked at closely. Since these tests showed that activated alumina is susceptible to large amounts of dissolution during the regeneration, this should be an item of extreme importance to evaluate in larger scale, multi-cycle tests. Headloss characteristics of various media sizes should be evaluated in order to make decisions regarding the use of higher capacity, smaller mesh sizes of alumina.

A major item that should be investigated is the disposal of regenerant wastes. In arid or semi-arid regions, evaporation ponds may be feasible. Otherwise, disposal may involve a separate, on-site treatment or hauling away by contract carriers. The costs associated with the disposal may be high.

SECTION 4

SELENIUM ANALYSIS STUDIES

ORGANIC SELENIUM

Gas chromatrography research was performed on three organoselenium indicator compounds chosen on the basis of their probability of occurrence in the soil environment and their commercial availability. Selenium substituted amino acids are likely to occur in a selenium contaminated soil but are likely to be quickly degraded. The three compounds chosen were dimethylselenide, diethylselenide, and dimethyldiselenide. Aqueous standards of these pure compounds were made up and they were analyzed by the dynamic headspace technique using nitrogen to strip the materials from the water. The method used was similar to that described by Bellar[15] for organohalides in water with the exception that the analytical column was five percent polyphenyl ether (five rings) on 60/80 mesh chromosorb W-HM and an FID detector was utilized. Testing showed that these organoselenium compounds were effectively stripped from the water and adequately captured by the adsorbent trap at relatively high concentrations. Interferring peaks which eluted at similar retention times to the organoselenium compounds prevented the realization of minimum detection limits less than about 100 ug/l. Extraction of these compounds by liquid-liquid extraction with n-pentane and analysis by electron capture detection showed that only the dimethyldiselenide compound was detectable but the minimum detection limit for this compound was 10-100 times better than with the dynamic headspace FID analysis.

Because of the poor minimum detection limits for these indicator organoselenium compounds, it appears that the technique will not be useful for drinking water analysis until further optimization of the technique can be performed.

ATOMIC ABSORPTION SPECTROPHOTOMETRY

The AAS technique remains as the most efficient and sensitive means for determination of total selenium. In the majority of the batch scale tests done, either selenium (IV) or selenium (VI) was tested by itself. Therefore, analysis of selenium could be done quickly on the AAS with the assumption that the total selenium present was either Se(IV) or Se(VI). In tests involving combined quantities of Se(IV) and Se(VI), the AAS determined total selenium concentrations and the fluorometric technique, described later, gave concentrations of Se(IV). Se(VI) was calculated by difference.

All total selenium analyses were done by the flameless atomic absorption technique on a Perkin-Elmer 305B AAS with a P.E. 2200 graphite furnace utilizing deuterium ultraviolet background correction and an electrodeless discharge selenium lamp. Standard conditions for the furnace were: a drying cycle of 30 seconds at 105 degrees C, a charring cycle of 10 seconds at 1000 degrees C, and an atomization cycle of 7 seconds at 2200 degrees C. Pyrolitically coated graphite tubes and the "max. power" function were used in analyses. This enabled a much lower atomization temperature and forced all available current into the furnace tube at a very fast rate, which is almost equivalent to instantaneous atomization.

An equal volume of 1000 ppm $Ni(NO_3)_2$ was added to the furnace after each sample was injected. This method is an EPA standard method.

When analyzing samples using the furnace technique, matrix interferences played an important role in determining the selenium present. The analyses of regeneration samples, which had high concentrations of sodium hydroxide and either sulfuric acid or hydrochloric acid, were greatly affected by the presence of these salts in the samples. Normally, standards of selenium were made using deionized water and concentrated nitric acid (the normal preservative for selenium). These standards were not usable with the regeneration samples, due to the marked difference in results when compared with standards made up from an approximate 0.05% sodium hydroxide selenium standard. Therefore, regeneration samples were diluted about 10:1 to 0.05% NaOH to negate any other interferences and then were analyzed using a comparative selenium standard made with 0.05% NaOH that was acidified with HNO_3 to a pH of less than 2.

To verify reproducibility and accuracy of these results, known amounts of selenium were spiked into regeneration samples. The analysis of the spiked samples showed concentrations that were equal to the sum of the known amount spiked and the unspiked sample within 10%. This accuracy is within the limits of the furnace technique. Table 2 shows these results.

The correction for matrix interferences was not necessary when concentrations of selenium exceeded 1.0 ppm. Above this level, selenium can be detected using the flame atomic adsorption technique and the flame technique is not subject to matrix interferences.

At the onset of testing, it appeared as though a double peak phenomena, presumed to be selenium (IV) and (VI), occurred when using uncoated tubes with no "max. power" input. Further work was conducted with more concentrated standards and the phenomena was not reproducible. It was suspected that some contamination was present in the reagents that was responsible for some of the peaks observed. Although this technique would have been the simplest method for differentiating Se(IV) and Se(VI), the idea was abandoned due to the inconsistent results. See Figures 3 and 4 for photographs of the AAS and associated equipment.

TABLE 2

VERIFICATION OF REPRODUCIBILITY FOR REGENERANT ANALYSIS*

Date	Initial Sample I.D.	Spiked Concentration (ppm)	Concentration (ppm)	Difference (ppm)
9-14	Col. 1	0.23	0.63	0.40
	Col. 2	0.28	0.70	0.42
9-26	Col. 1	0.46	0.82	0.36
	Col. 2	0.44	0.83	0.39

*24 ml's of sample were added to 1 ml of 10 ppm selenium standard to give a spiked concentration of 0.40 ppm. The differences noted above are with 10% of this value.

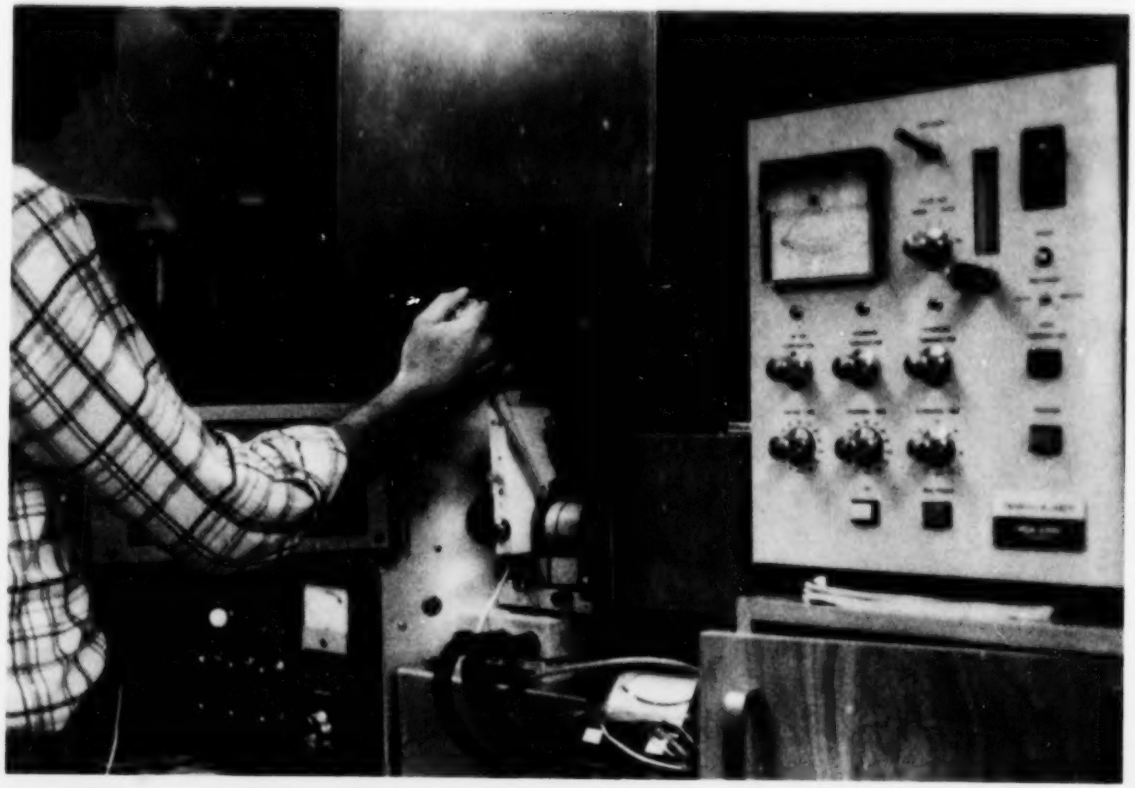


Figure 3. Injecting a sample into the A.A.S. furnace.

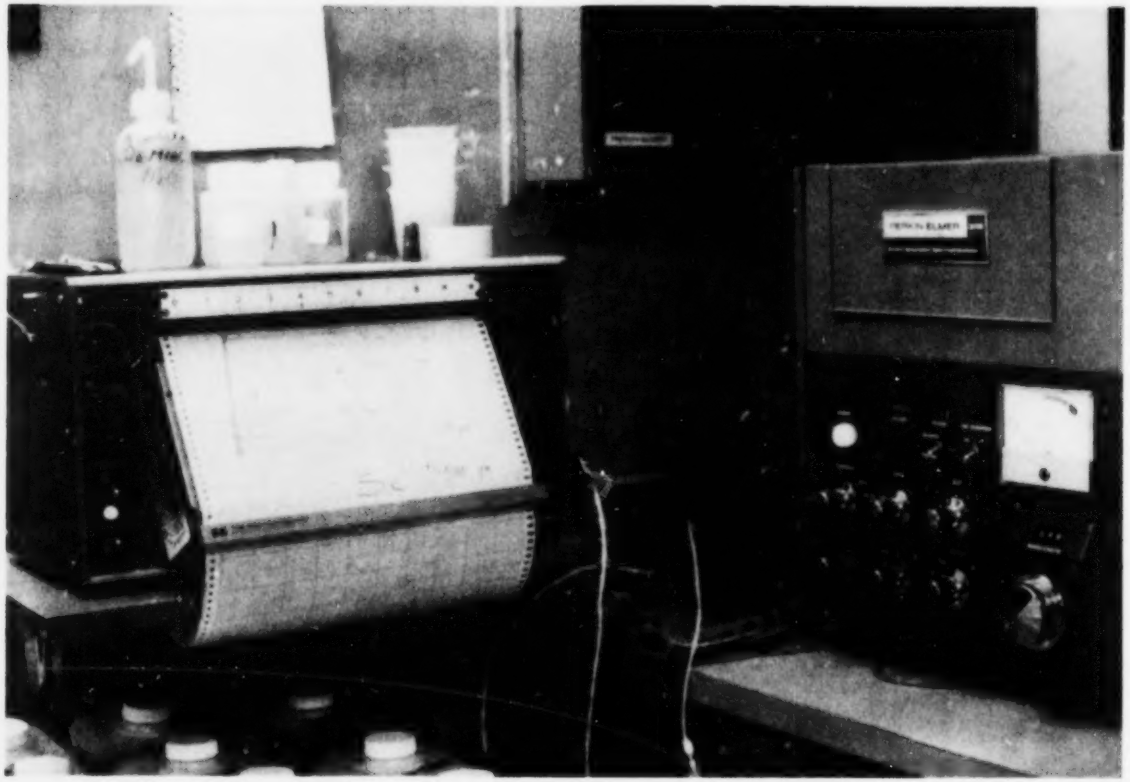

PERKIN ELMER

Figure 4. A.A.S. strip chart recorder.

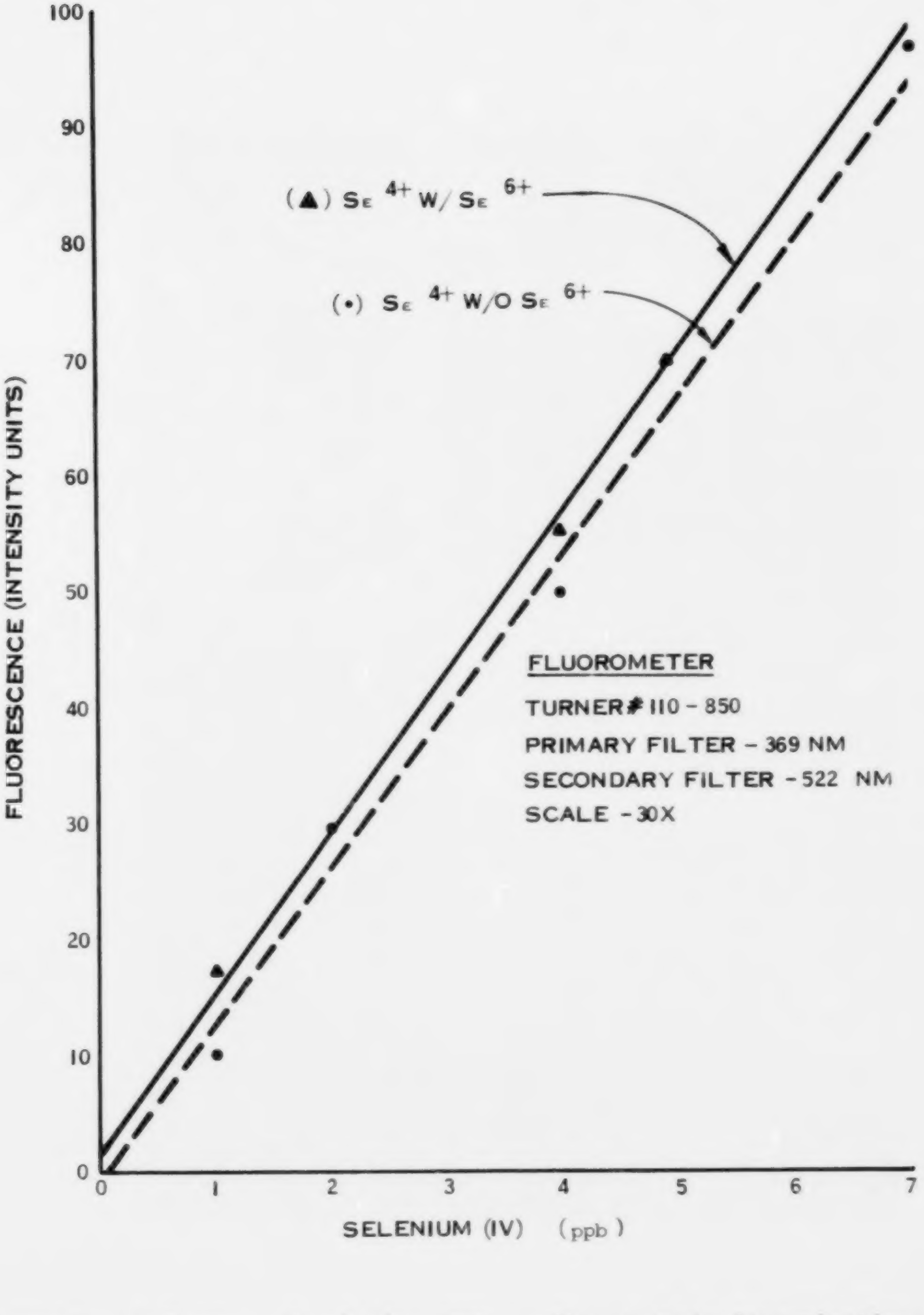


Figure 5. Influence of selenium (VI) on fluorometric determination of selenium (IV), 0 - 7 ppb.

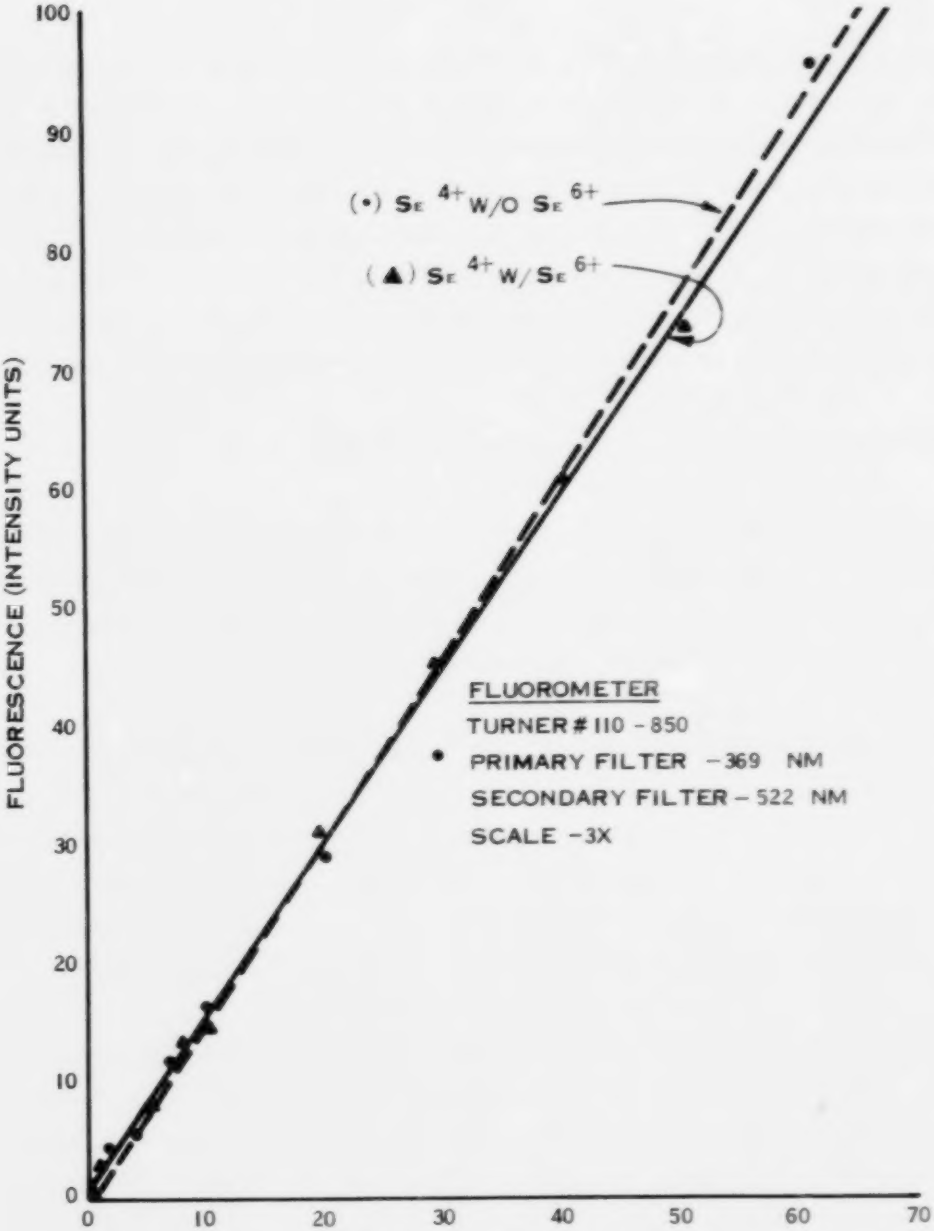


Figure 6. Influence of selenium (VI) on fluorometric determination of selenium (IV), 0 - 70 ppb.

COLORIMETRIC DETERMINATION OF SELENIUM (IV)

The Standard Methods diamino benzidine method for selenium is selective for selenium (IV) if the permanganate oxidation and subsequent reduction steps are omitted from the procedure. This technique has shown to produce precise results, but the presence of selenium (VI) produces a slight interference. The accuracy of this test with selenium (VI) present is somewhat less than that of the fluorometric technique (discussed next). But, this technique is useful in the selective determination of selenite. It was not used in this study because the analysis requires approximately one liter of sample and is much more time consuming than the fluorometric technique.

FLUOROMETRIC DETERMINATION OF SELENIUM (IV)

Selenious acid (H_2SeO_3) reacts with 2,3 diaminonapthalene in an acid solution to form the strongly fluorescent naptha-(2,3-d)-2-selena-1,3-diozole. Selenates (Se(VI)) are not reduced to selenites (Se(IV)) under the conditions of this analysis, hence this method is specific only for selenium in the four-valence state.

This technique, as described by Raihle[16], was tested as a means to differentiate the two forms of inorganic selenium in removal tests performed with combined selenium (IV) and (VI) present and to determine the amount of Se(IV) present in some well water samples that were analyzed for selenium. Plots of fluorescent intensity versus concentration of selenium (IV) in the range of 0 to 70 ppb are linear and are practically free from selenium (VI) interferences, as shown in Figures 5 and 6.

Standards of known concentrations of selenium (IV), as verified by the AAS, were analyzed using this technique and the calibration curves (Figures 5 and 6) were then drawn. Similar standards of Se(IV) were spiked with varied amounts of Se(VI) and the results are plotted alongside the curves without Se(VI) present. The curves are identical within experimental error.

This technique is much more convenient to use than the colorimetric technique. 10 ml of sample is required, compared to 1 liter needed to analyze samples colorimetrically. Also, to analyze 10 samples fluorometrically requires approximately six hours, which is about one-quarter of the time that it takes to do 10 samples colorimetrically. All fluorometric analyses were performed with a Turner Model 110 Filter Fluorometer with a standard lamp (#110-850). The samples were analyzed at an excitation frequency of 369 nm (primary filter #110-811) and had a fluorescence emission maximum of 522 nm (secondary filter #110-822). See Figure 7 for a photograph of the fluorometer.

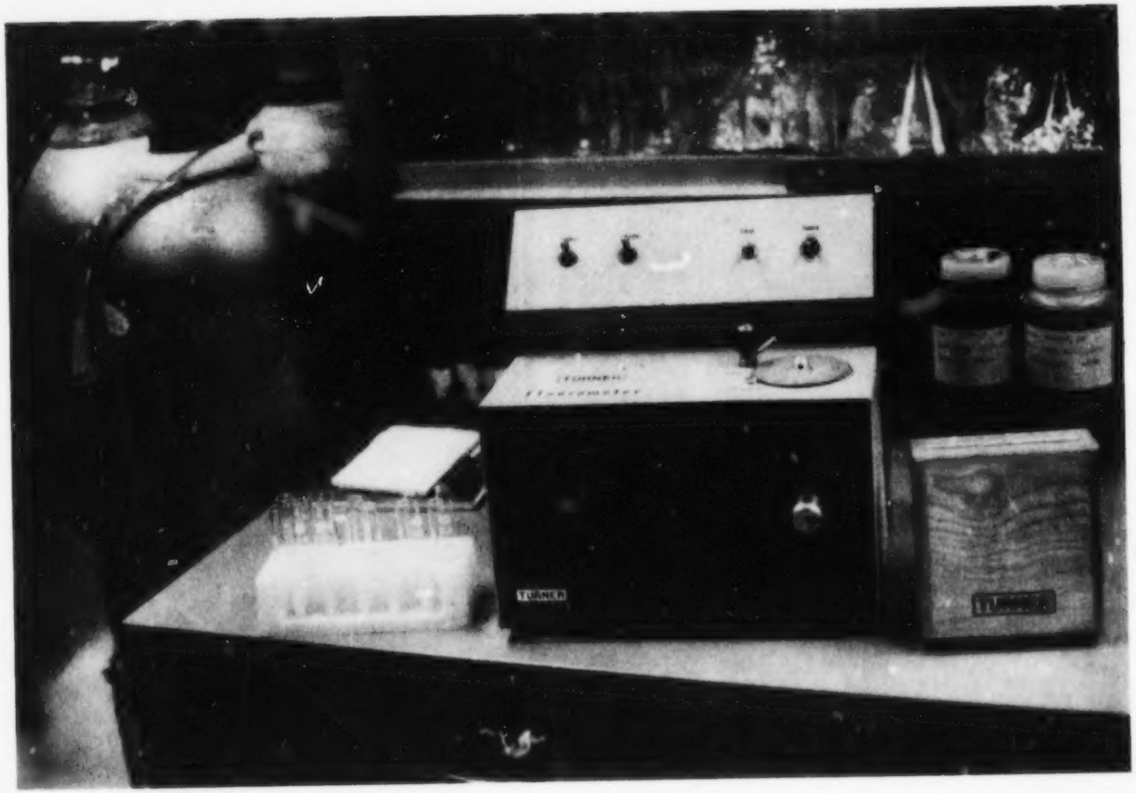

TURNER
Fluorometer
TURNER

Figure 7. Fluorometer.

SECTION 5
SELENIUM BATCH STUDIES

As described in the introduction, a series of bench scale adsorption isotherm studies were undertaken to analyze the various parameters involved in the use of activated alumina to remove selenium. Studies of regeneration techniques, kinetics, pH effects, mesh size, selectivity effects of various anions and cations, and capacities were performed to develop the conceptual information necessary for the efficient design of activated alumina contactors.

All batch scale studies were performed with deionized water spiked with selenium (IV) and/or selenium (VI) as the stock solution. No other species were added to the matrix, except in the case of studies involving pH effects, ion interferences, and relative selectivity.

All batch studies, with the exception of some pH tests, were performed in 250-ml ehrlenmeyer flasks with glass stoppers. Contact was achieved by mixing with a Labline "Junior Orbit Shaker" at 200 rpm. Control flasks containing the selenium stock solution without activated alumina showed no loss of selenium during the tests. It was assumed that the glassware utilized did not absorb significant amounts of selenium within the timeframe of the tests. See Figure 8 for a photograph of the shaking apparatus.

REGENERATION

Various regeneration techniques involving the use of acids and bases were employed to prepare virgin activated alumina for selenium sorption. In all of the batch studies, only virgin activated alumina were used. No actual regeneration of selenium-saturated activated alumina was done during this phase of the study. Rather,

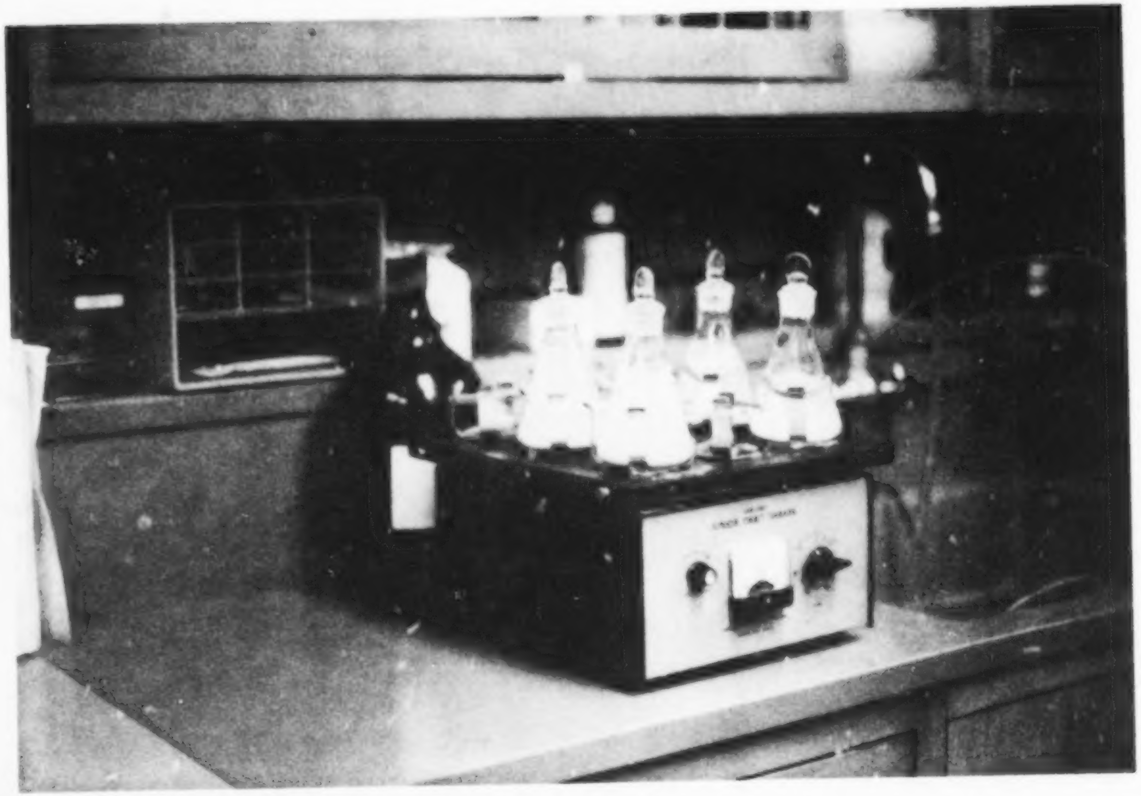


Figure 8. Shaking apparatus.

the expected regeneration techniques to be used in column studies were modeled by preparing fresh out-of-the-can activated alumina with bases and acids to develop optimal adsorption characteristics.

Figure 9 shows the relationship of selenium removal versus activated alumina contact time with a one percent solution of sodium hydroxide (1% NaOH). Fresh activated alumina was rinsed with this basic solution for various amounts of time to test the effect of NaOH rinse time on capacity for selenium removal. This technique has been suggested by various authors who have used activated alumina to remove the chemically similar anions, arsenic, and fluoride[2,6,7,13].

Activated alumina exhibits the highest selectivity for hydroxide (OH^-) ions. This caustic rinse should remove all other anions present in or on active sites on the alumina and replace them with hydroxide ions.

As is seen from the graph, selenium removal efficiencies of 90 percent are achieved with as little as five minutes of rinsing. In all the following batch scale tests, a 50 minute rinse with 1 percent NaOH was used with fresh activated alumina to ensure optimum removals of selenium.

Following the caustic rinse, a 5-minute rinse with 150 ml of deionized water was found to be necessary as an intermediate step between base and acid rinses. Without this rinse, the exothermic acid-base reaction tended to alter the activated alumina and bind it in clumps.

The next step in the regeneration procedure is to rinse the now basic alumina bed with an acid to lower the pH, essentially to remove the OH^- ions from the sites on the alumina. As previously suggested by Ball[2], hydrochloric acid (HCl) and sulfuric acid (H_2SO_4) were utilized to compare their abilities to prepare the activated alumina for selenium (IV) and (VI) removal. Figure 10 plots the relationship of selenium ((IV) or (VI)) removal versus activated alumina contact time with 0.05 N solutions of HCl or H_2SO_4. This concentration of acid was taken from Ball's work. Prior to this acid rinse, the fresh activated alumina had been initially rinsed for 50 minutes with 1 percent NaOH, then with deionized water for 5 minutes.

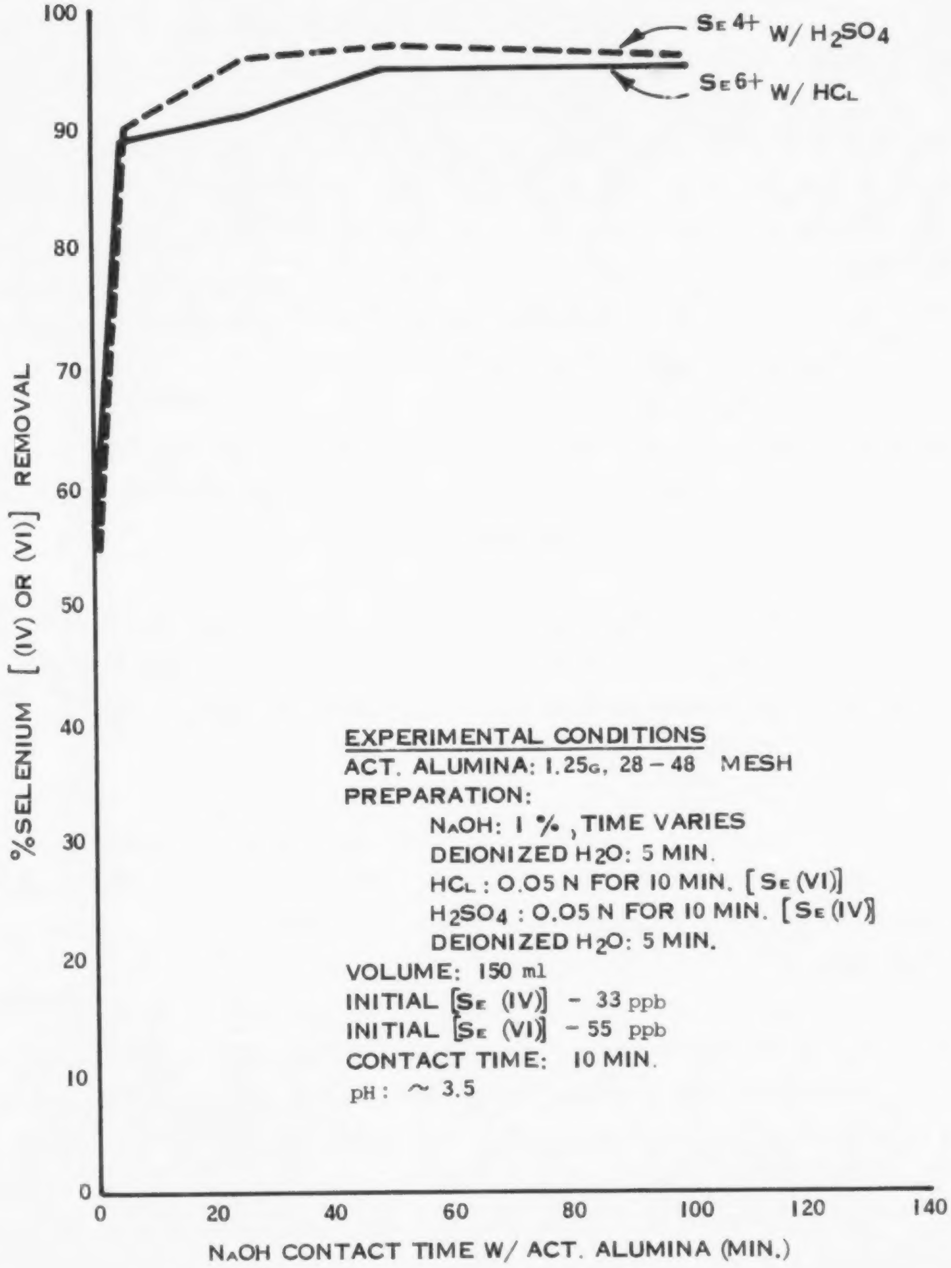


Figure 9. Initial preparation of fresh activated alumina with NaOH.

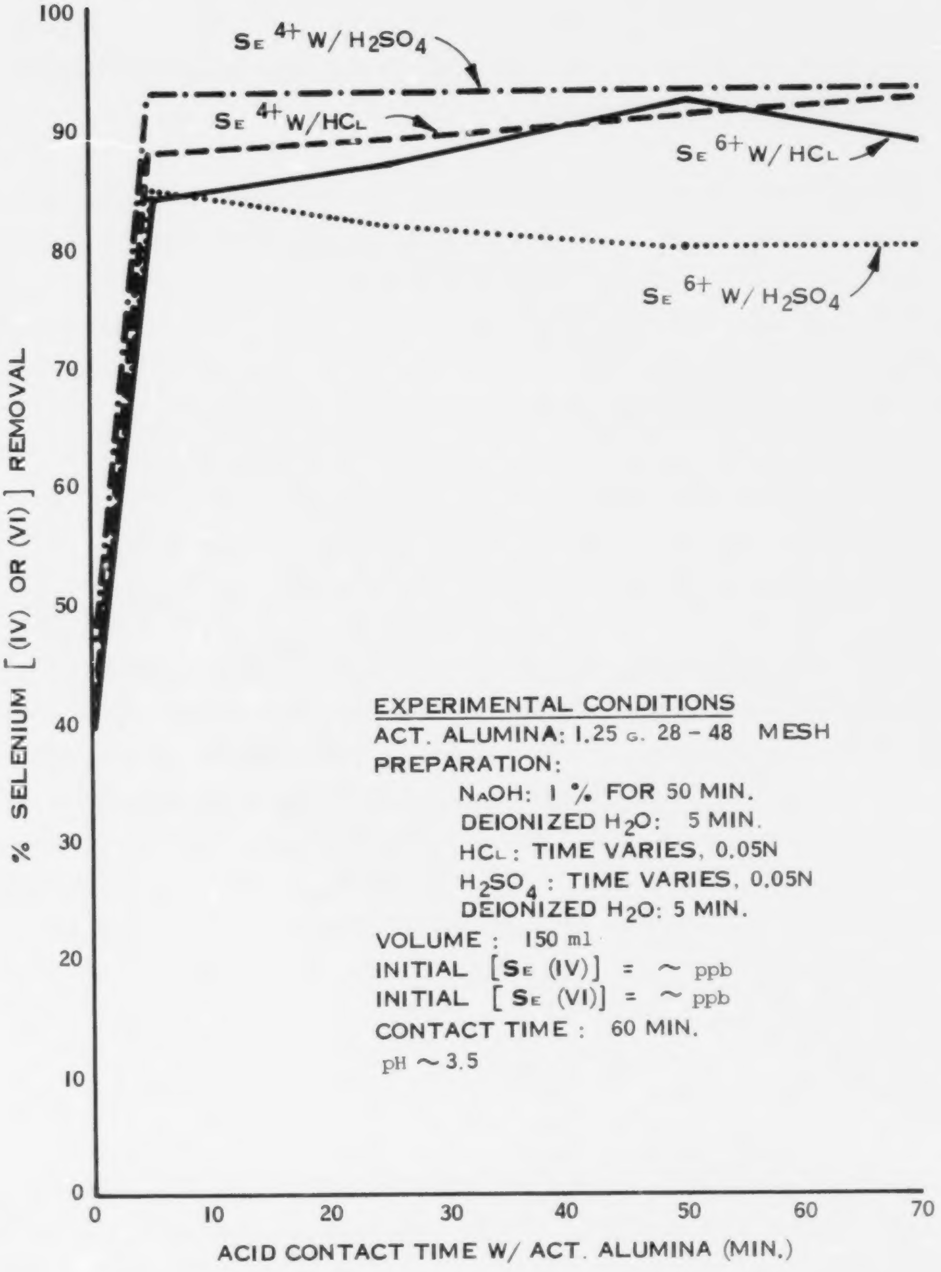


Figure 10. Initial preparation of fresh activated alumina with acid after NaOH rinse.

It appears that there are no differences in the removal capabilities of selenium (IV) with activated alumina rinsed with HCl or H_2SO_4. Because slightly better removals of Se(IV) were achieved with H_2SO_4, this acid rinse was used in all the following tests involving selenium (IV) removal.

Figure 10 also shows that the HCl rinse works better in preparing activated alumina for selenium (VI) removal than the H_2SO_4 rinse. This is thought to be because the sulfate ion (SO_4^{2-}) from the H_2SO_4 actively competes for sites on the activated alumina with the aqueous form (SeO_4^{2-}) of selenium (VI). The chloride ion (Cl^-) does not compete like the sulfate with selenium (VI). Therefore, an HCl rinse was used in all the following tests involving selenium (VI) removal.

On the basis of these experiments, a 10 minute rinse with either 0.05 N HCl or 0.05 N H_2SO_4 was used in all the batch scale tests from this point on. This contact time allows for optimum selenium removals.

Following the acid rinse, the pH of the activated alumina bed was adjusted to achieve a consistent pH of 4.0 during the removal tests, except to determine the relative selectivity of competing ions. Depending on the amount of activated alumina used and the type of acid rinse used, two to four 5 minute rinses with deionized water were required to reach pH = 4.0. For most of the tests, 1.25 grams of activated alumina were used and, with either H_2SO_4 or HCl rinses, three five-minute rinses were required. Five or more deionized water rinses did not produce any appreciable pH change above pH = 4.0. The greatest pH change occurred within the first three deionized water rinses.

KINETICS

The kinetics of sorption of the two selenium forms were determined to delimit the range of flow rates suitable for the activated alumina process. This testing also helped to determine the contact times to be used in batch scale studies. Individual flasks, each with the same amount of prepared activated alumina, were used for each separate time period tested, between 0 and 120 minutes.

As seen in Figure 11 a great majority of selenium removal occurs in the first ten minutes of contact with activated alumina. Rubel[13] suggests this optimum contact time in his work on fluoride removal. However, removal still seems to be taking place for upwards of 60 minutes in the case of selenium (IV). For this reason, a 60-minute contact time with the stock selenium solution was employed in all batch scale tests. This ensured equilibrium between the remaining selenium in solution and the activated alumina.

The 28-48 mesh size activated alumina was used in these tests. It was assumed that the different mesh sizes would remove selenium at different rates, but that at equilibium, the mesh size should not affect the total amount of selenium removed in the batch scale.

Previous investigators have conducted isotherm tests to determine the capacity for removal of fluoride and arsenic anions using activated alumina[6,7,10.]. They have shown that contact times on the order of 48 hours are required to reach equilibrium. Gupta and Chen[6] used an initial concentration of 4.0 mg/l arsenic with a dose of 2 g/l activated alumina. Choi and Chen[10] used an initial concentration of 25 mg/l fluoride with a dose of 25 g/l activated alumina to determine kinetics. Both of these tests used an initial concentration much greater than was used in this study. With C_o = 0.10 mg/l and a dose of 8.3 g/l activated alumina, the ratio of initial concentration of contaminant to dose of activated alumina is 0.012 mg/g. This is nearly 100 times less than the ratio of 1 mg/g for the fluoride study. Since the intensity of adsorption is considered to be very dependent on the concentration of the contaminant, the results of this study appear to be well within reason.

pH EFFECTS

The influence of pH on the sorption of selenite and selenate was investigated in batch tests covering the range of pH values commonly occurring in potable waters. As a first step in determining the effect of pH on selenium adsorption by activated alumina, the pH of the stock selenium solution was adjusted to the desired value with NaOH or HCl and then put in contact with the prepared activated alumina for 60 minutes. Figure 12 shows the results. As can be seen, the final pH (pH_f) of the

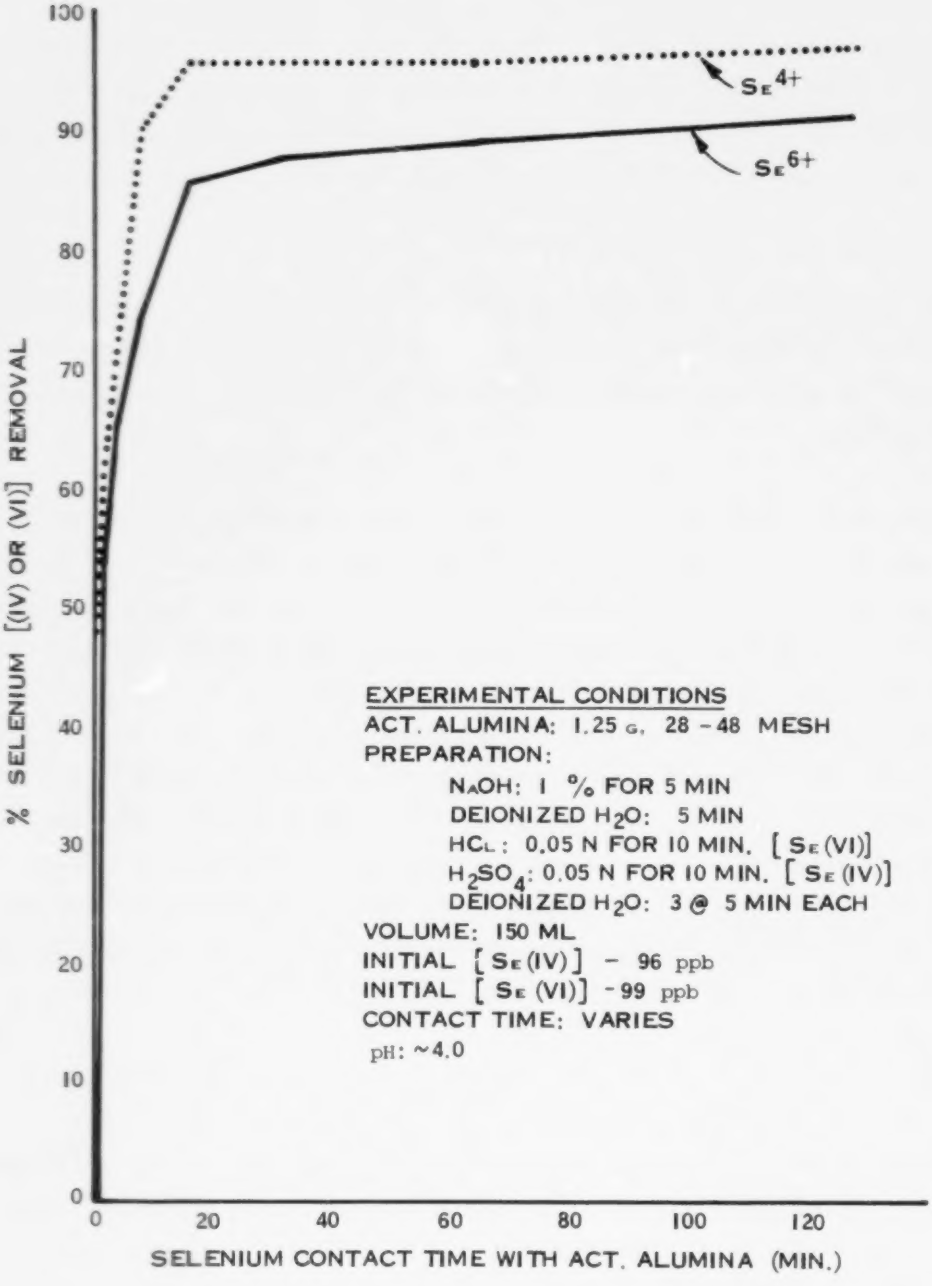
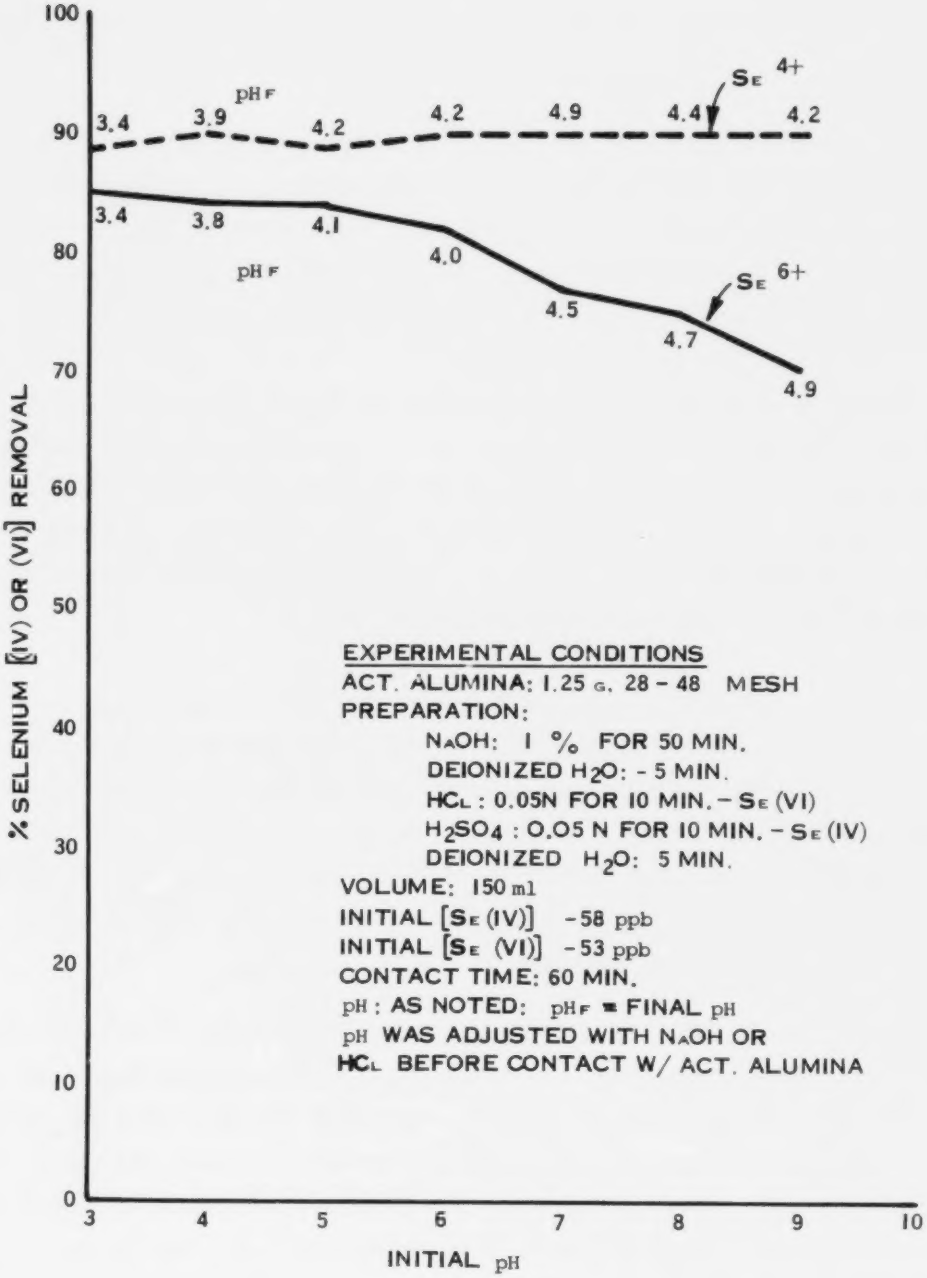


Figure 11. Effect of contact time with activated alumina on selenium adsorption.



EXPERIMENTAL CONDITIONS

ACT. ALUMINA: 1.25 G. 28 - 48 MESH

PREPARATION:

- NaOH: 1 % FOR 50 MIN.
- DEIONIZED H_2O: - 5 MIN.
- HCL : 0.05N FOR 10 MIN. - Se (VI)
- H_2SO_4 : 0.05 N FOR 10 MIN. - Se (IV)
- DEIONIZED H_2O: 5 MIN.

VOLUME: 150 ml

INITIAL [Se (IV)] -58 ppb

INITIAL [Se (VI)] -53 ppb

CONTACT TIME: 60 MIN.

pH : AS NOTED: pHF = FINAL pH

pH WAS ADJUSTED WITH NaOH OR HCL BEFORE CONTACT W/ ACT. ALUMINA

Figure 12. Effect of initial pH on adsorption of selenium.

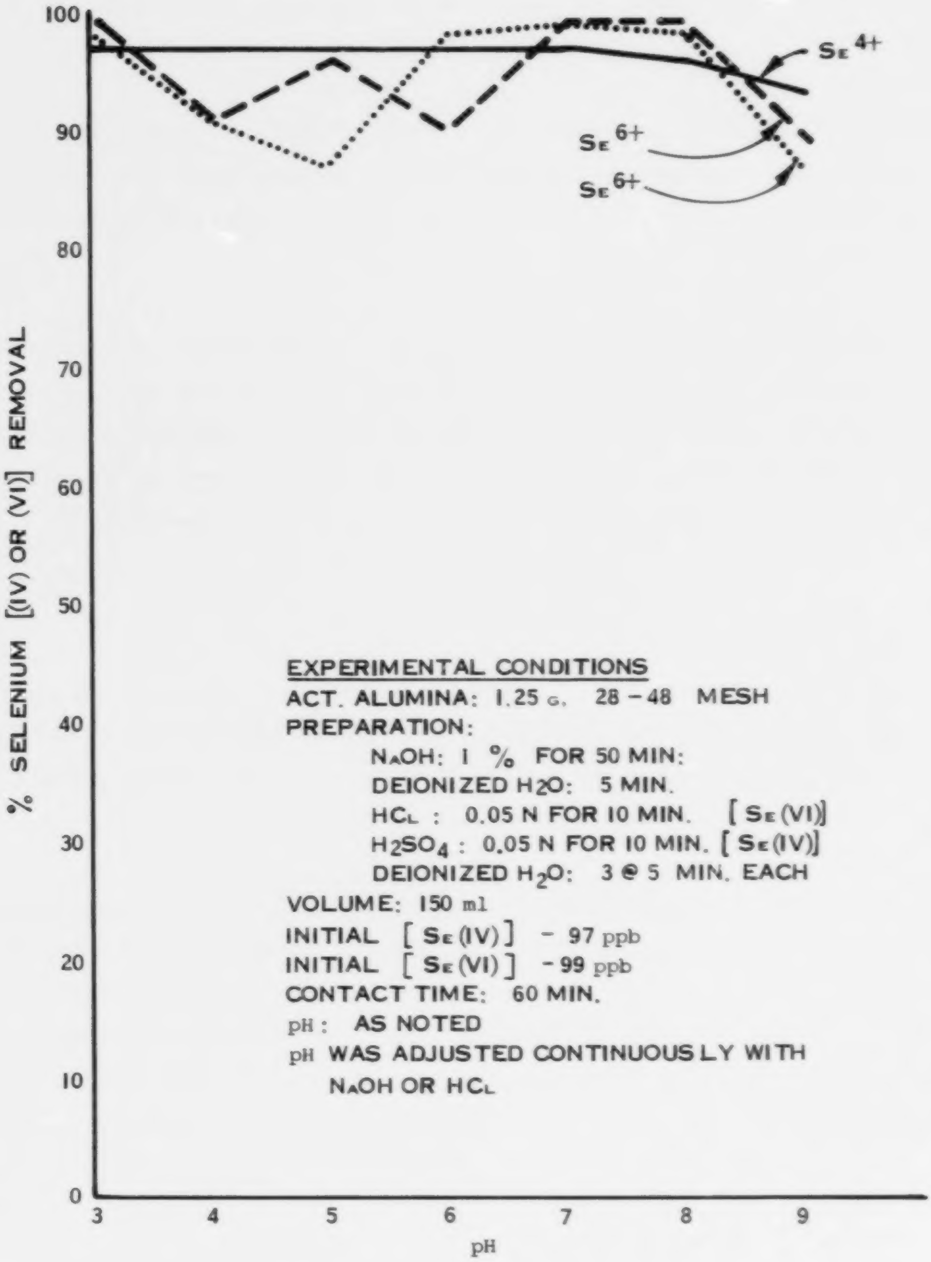
solution changed radically from the initial pH. At no time were we able to maintain a constant pH in the solution during any of the initial pH studies, except in the range of pH = 4.0.

The data does show a trend, though. In the small variation of pH in the selenium (IV) tests, pH seemed to have little effect on Se(IV) adsorption. However, the slight changes in pH noticed in the selenium (VI) tests seemed to indicate a relationship between lower pH and increased removal. But, this difference is probably due to the interference of OH^- ions added to adjust the pH upward.

Our inability to maintain a constant pH during the 60 minutes of contact time with the activated alumina led us to look at buffers that could maintain a constant pH without interfering with adsorption. Different buffers comprised of pthalate, acetate, borate, and phosphate were tried for different pH's and they all interfered with selenium (IV) and (VI) adsorption. Their presence in the sample also interfered with the atomic absorption spectrometry analysis of selenium.

The next approach to maintaining a constant pH during contact with the activated alumina was to continously monitor and adjust the pH using a jar testing apparatus to provide the mixing. The activated alumina was prepared as usual in the ehrlenmeyer flasks, then it was transferred to 1000 ml beakers with the stock selenium solution. The pH was monitored continously and was adjusted by the dropwise addition of either 0.1 N NaOH or 0.1 N HCl. The pH was allowed to deviate plus or minus 0.2 pH units before any adjustment was done.

Figure 13 shows the results of the testing. Adsorption of selenium (IV) by activated alumina was not effected by pH less than 7. At pH 8 and 9, slightly lower removals were observed. This was probably related to the fact that the dominant species of Se(IV) in solution changes from $HSeO_3^-$ to $SeO_3^=$ at about pH 8 and greater amounts of NaOH were added to maintain these pH's. As can be seen, pH had a varied effect on selenium (VI) adsorption. Removal appears to be higher at low pH (3), drops at slightly higher pH, then suddently increases again to reach a higher removal at pH 7. Removal tends to drop off as pH is increased above 7. It is most likely that the addition of NaOH caused interferences that hindered Se(VI) adsorption. Two separate tests were done with Se(VI) and Figure 13 shows the variability.



EXPERIMENTAL CONDITIONS

ACT. ALUMINA: 1.25 G. 28 - 48 MESH

PREPARATION:

NaOH: 1 % FOR 50 MIN:

DEIONIZED H_2O: 5 MIN.

HCl : 0.05 N FOR 10 MIN. [Se(VI)]

H_2SO_4 : 0.05 N FOR 10 MIN. [Se(IV)]

DEIONIZED H_2O: 3 @ 5 MIN. EACH

VOLUME: 150 ml

INITIAL [Se(IV)] - 97 ppb

INITIAL [Se(VI)] - 99 ppb

CONTACT TIME: 60 MIN.

pH : AS NOTED

pH WAS ADJUSTED CONTINUOUSLY WITH NaOH OR HCl

Figure 13. Effect of constant pH on adsorption of selenium.

Because activated alumina is an amphoteric material, pH should be an important factor in determining its capacity as an adsorbent. These tests fail to show this phenomena.

Ball's[2] work showed a great dependence on pH for Se(IV) and Se(VI) adsorption by activated alumina. Adsorption increased almost linearly from pH 7 to 4, with adsorption "peaking out" at approximately pH 3. This is the type of phenomena that would be expected.

All further batch tests were done at pH = 4.0. No adjustment was necessary to achieve this pH and, from this data, pH had no effect on selenium (IV) adsorption in the batch mode. It was later determined that the pH of the activated alumina could be adjusted by rinsing with a less concentrated acid. This was done in the selectivity series tests and could be used to repeat the pH experiments just mentioned.

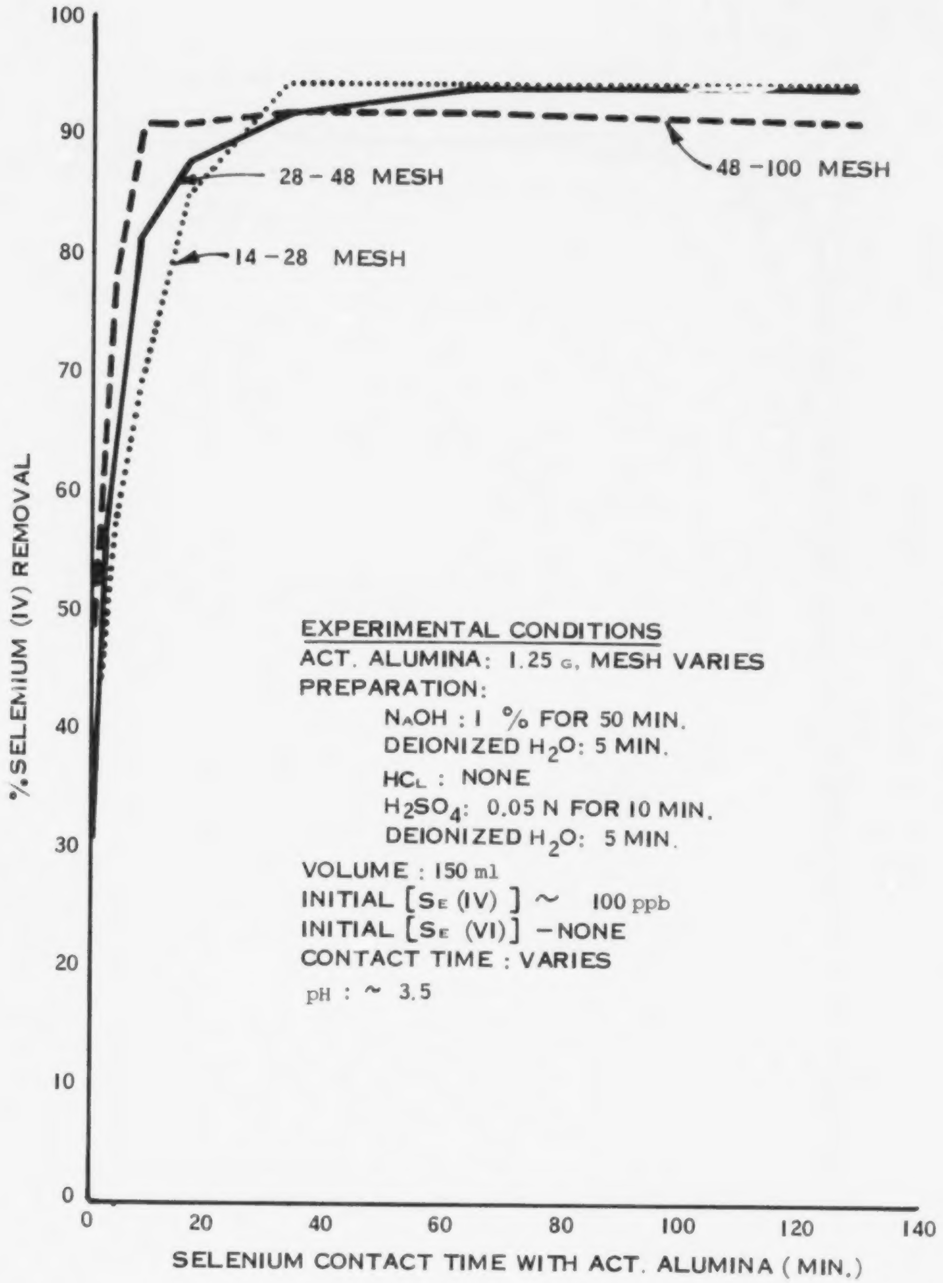
MESH SIZE

The effect of activated alumina mesh size on selenium sorption efficiency was determined for the following medias: 14-28, 28-48, and 48-100 (arranged in order from largest to smallest). These are three of the four mesh sizes typically produced. A larger size, 8-10 mesh, is also available, but was not evaluated.

Figure 14 shows the relationship between selenium (IV) removal and contact time with the three sizes of activated alumina. As expected, the smaller mesh size, 48-100, removes selenium (IV) faster than the other two sizes due to its larger surface area per unit weight. In actual activated alumina contacts, a 5-minute contact time through the bed might be chosen as a median value for a cost-effective residence time. Comparing removals of the three mesh sizes at 5 minutes contact time gives us:

14-28 - 59% Se(IV) removal
28-48 - 68% Se(IV) removal
48-100 - 81% Se(IV) removal

Figure 15 shows selenium (VI) removal versus contact time with the three sizes of activated alumina. As expected, the smaller mesh size removes selenium (VI)



EXPERIMENTAL CONDITIONS

ACT. ALUMINA: 1.25 G, MESH VARIES

PREPARATION:

NaOH : 1 % FOR 50 MIN.

DEIONIZED H_2O: 5 MIN.

HCL : NONE

H_2SO_4: 0.05 N FOR 10 MIN.

DEIONIZED H_2O: 5 MIN.

VOLUME : 150 ml

INITIAL [Se (IV)] ~ 100 ppb

INITIAL [Se (VI)] - NONE

CONTACT TIME : VARIES

pH : ~ 3.5

Figure 14. Effect of mesh size on removal of selenium (IV).

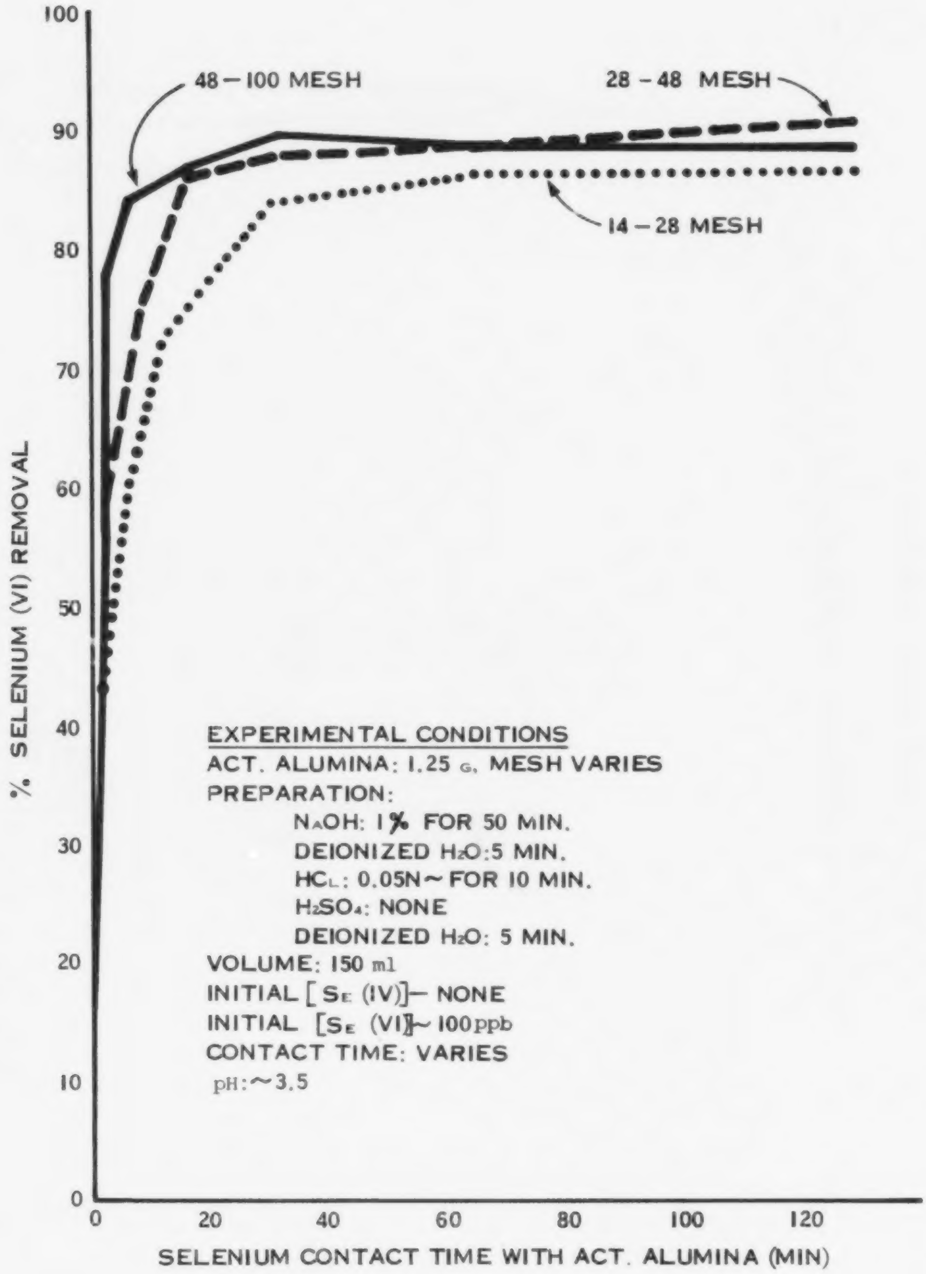


Figure 15. Effect of mesh size on removal of selenium (VI).

faster. Again, comparing removals of the three mesh sizes at 5 minutes contact time gives us:

14-28 - 54%
28-48 - 65%
48-100 - 80%

While the smaller mesh size (48-100) provides faster removal, one must consider design constraints in constructing a full scale removal facility. The larger mesh size would be more difficult to fluidize during backwash, but could allow longer run lengths if headloss is involved as a limiting factor. A trade-off would have to be made between removal efficiencies, run length, and backwash volumes in the final design of a full-scale removal facility. The most practical size is probably a 28-48 mesh.

INTERFERING IONS

The effect of various anions and cations on the selenium sorption capacity of activated alumina was investigated. Specific anions of interest were chloride, bicarbonate, sulfate, and nitrate. Specific cations of interest were calcium, magnesium, and sodium.

Figure 16 depicts the relationship between concentration of the various anions and removal of selenium (IV). No great effect is seen by any of the anions introduced in concentrations less than 50 mg/l. Greater concentrations of the anions produce a slight decrease in efficiency of removal, with the exception of bicarbonate (HCO_3^-). This ion has a more pronounced effect on activated alumina's ability to adsorb selenium (IV), but this may be an artifact of the effect of pH on the form of Se(IV). All anions were added as a salt of sodium (Na), because sodium is expected to have minimal interferences with adsorption.

Figure 17 shows how the chosen anions effect the removal of selenium (VI). For concentrations of 25 mg/l of all the anions, an apparent increase in removal efficiency was noted. It is difficult to say if a real trend exists at these low levels, because certainly one would not expect enhancement of adsorption by the presence of other

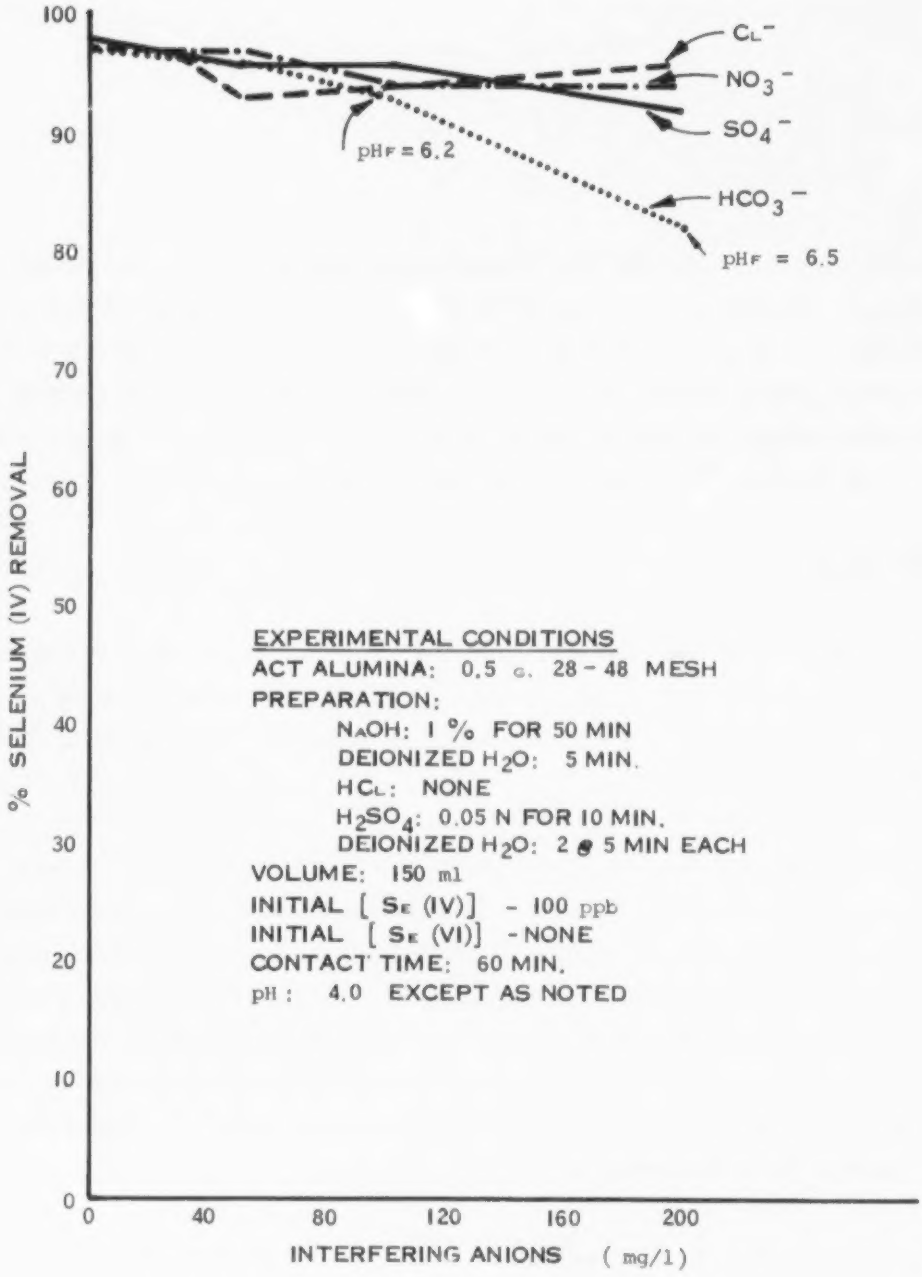
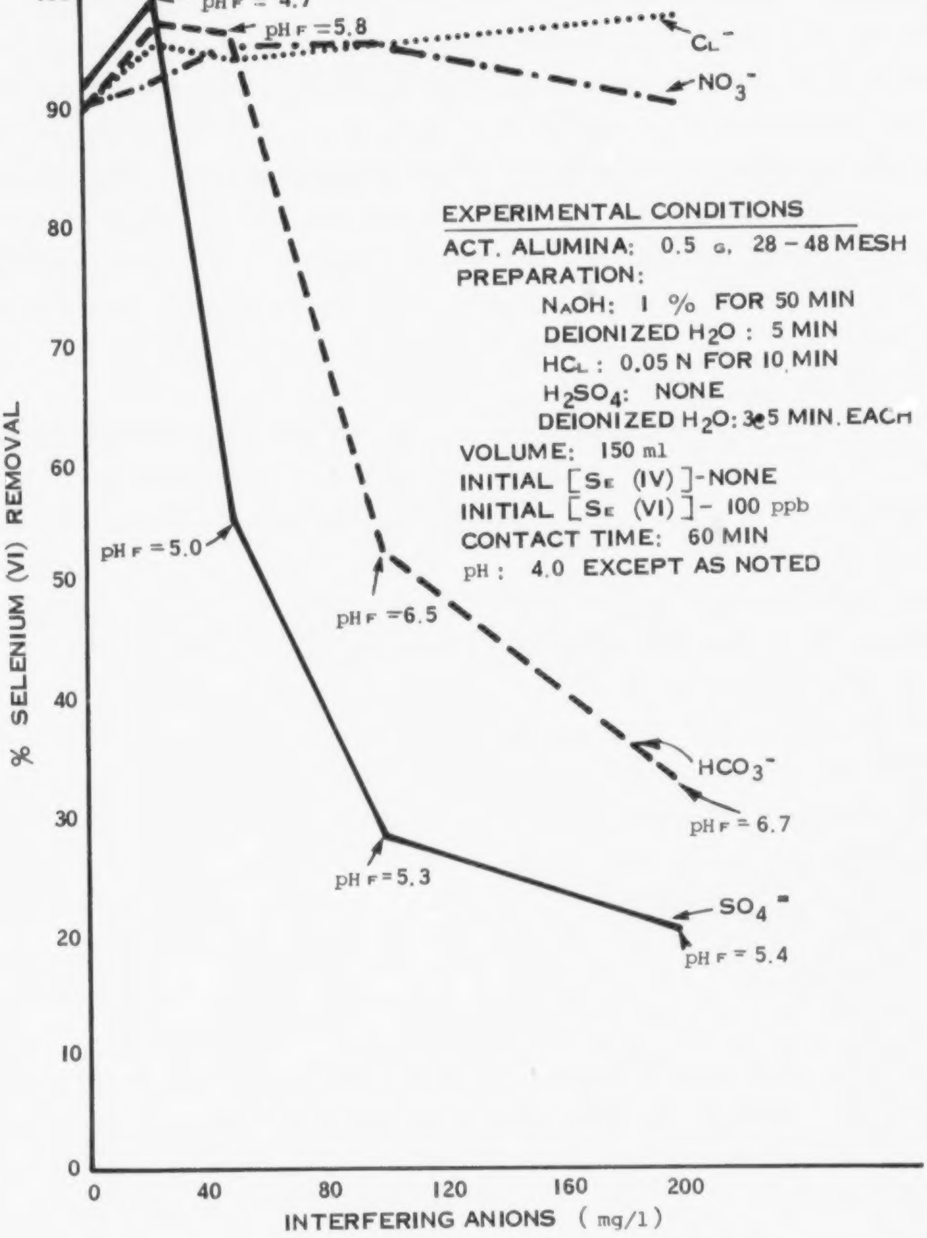


Figure 16. Influence of various anions on adsorption of selenium (IV).



EXPERIMENTAL CONDITIONS

ACT. ALUMINA: 0.5 G, 28 – 48 MESH
PREPARATION:
NaOH: 1 % FOR 50 MIN
DEIONIZED H_2O : 5 MIN
HCL : 0.05 N FOR 10 MIN
H_2SO_4: NONE
DEIONIZED H_2O: 3×5 MIN. EACH
VOLUME: 150 ml
INITIAL [SE (IV)]-NONE
INITIAL [SE (VI)]- 100 ppb
CONTACT TIME: 60 MIN
pH : 4.0 EXCEPT AS NOTED

Figure 17. Influence of various anions on adsorption of selenium (VI).

anions. Perhaps the lower concentrations calculated in these flasks were due to matrix interferences from the anions added. However, at high concentrations, sulfate (SO_4^{2-}) and bicarbonate (HCO_3^-) interfered greatly. As mentioned previously, sulfate is expected to heavily compete with selenium (VI) for sites on activated alumina since they are chemically very similar and because of activated alumina's alumina preference for sulfate over selenate. Other researchers have noted bicarbonate's interference with adsorption of ions similar to selenium, but the mechanism is unclear. The presence of high alkalinity in raw water will hinder the removal of both selenium (IV) and (VI), though it will have a greater effect on selenium (VI) removal. Nitrate and chloride exhibit little interference of adsorption.

In the next test, the cations Mg^{++}, Ca^{++} and Na^+ were added to the stock solutions of selenium (IV) and (VI) as salts of chloride (Cl) because, from the anion interference tests, chloride seemed to exhibit less interference than the other anions.

As expected, the cations shows little tendency to inhibit selenium (IV) adsorption. Figure 18 shows little change in the removal of selenium (IV) with varied doses of cations. However, addition of varied amounts of cations to the selenium (VI) stock seemed to enhance adsorption slightly. As is shown in Figure 19 removals rise from about 90 percent with no cations present to about 98 percent with 200 mg/l of calcium and magnesium present. This phenomena may be an artifact of the matrix interferences, but it may also be due to the "secondary adsorption" phenomena explained in the introduction.

SELECTIVITY SERIES

Kubli's original selectivity series for adsorption of anions by activated alumina included many more ions than those listed in Section 1. The complete list includes the following anions, in order of decreasing preference: OH^-, PO_4^{3-}, $C_2O_4^{2-}$, F^-, (SO_2^{2-}, $(Fe(Cn)_6)^{4-}$, CrO_4^{2-}), $S_2O_3^{2-}$, SO_4^{2-}, ($(Fe(CN)_6)^{3-}$, $Cr_2O_7^{2-}$), (NO_2^-, CNS^-), I^-, Br^-, Cl^-, NO_3^-, MnO_4^-, ClO_4^-, CH_3 COO^-, S^{2-}.

His method for determining the selectivity series was to introduce a solution containing two competing anions into a very narrow column filled with activated

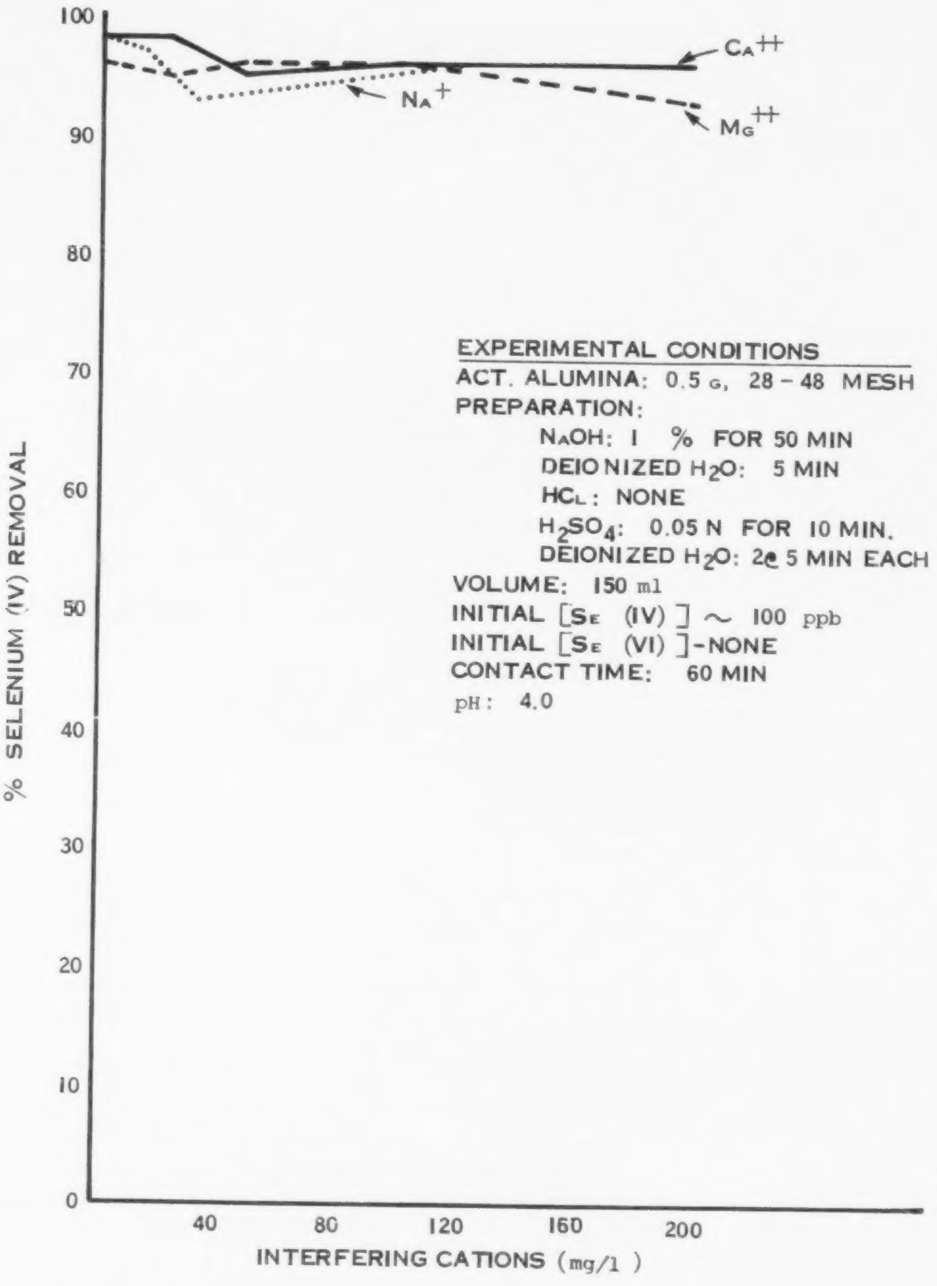


Figure 18. Influence of various cations on adsorption of selenium (IV).

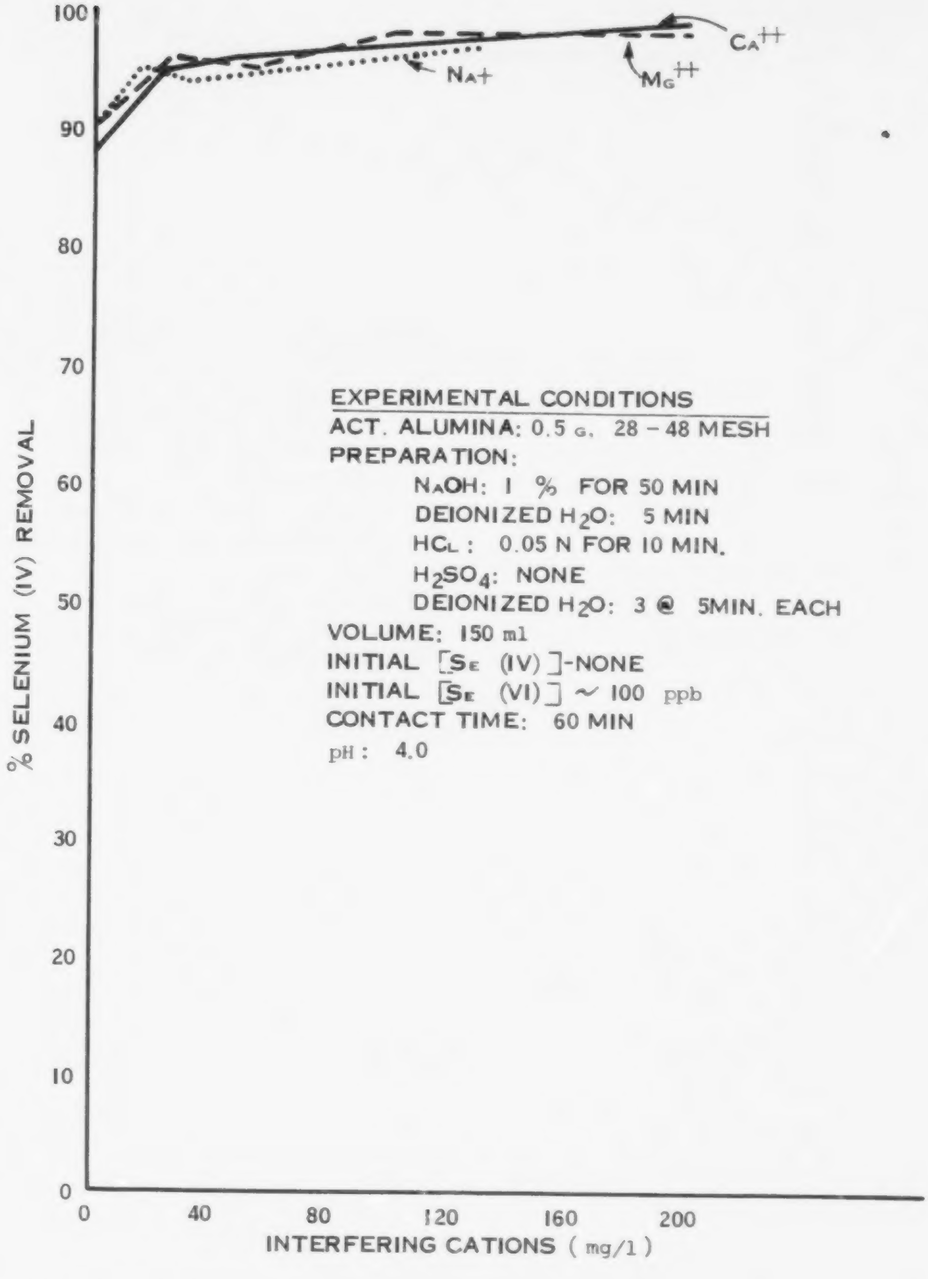


Figure 19. Influence of various cations on adsorption of selenium (VI).

alumina which had been rinsed with 1:1 perchloric acid. The solution was "filtered" through the column and the relative position in the column was detected by the use of a developer which produced specific color changes depending on the species present. The anion found in the top part of the column was determined to be the more preferred ion.

In this study, equal molar amounts of competing species were put in solution with identically pretreated alumina at a pH of approximately 6.5 and contacted by the normal method. By determining the percent of each species removed, the greater removed species was assumed to be more preferred by activated alumina. The ions of interest were:

$HSeO_3^-$ (Se(IV)), $SeO_4^=$ (Se(VI)), H_3AsO_3 (As(III)), $H_2AsO_4^-$ (As(V)),
F^-, $H_2PO_4^-$, SO_4^-, HCO_3^-, Cl^-, NO_3^-.

Two and one-half grams of activated alumina, when contacted for 1 hour with 150 ml's of Se(IV) containing 5.0 mg/l, was found to remove approximately one-half the selenium. This amount of alumina was chosen to do the remaining tests. 5.0 mg/l Se(IV) corresponds to a concentration of $6.3x10^{-5}$ M. This molar concentration was used for all competing species. The preparation of each batch of activated alumina was pretreated the following way:

50 minutes, 1% NaOH, 200 ml
5 minutes, D.I. water, 200 ml
3-10 minute rinses, 0.001 N HCl, 200 ml
2-5 minute rinses, D.I. water, 200 ml

In the two competition tests with the chloride ion, 0.001 N $HClO_4$ was used as the acid rinse. HCl was used in most of the tests because it would appear that hydrochloric acid may be the acid used in an actual treatment facility.

To reduce the number of tests, we prepared an estimated selectivity series and tested two consecutive species in the list to verify our hypothesis, starting with the most preferred ion. If the preferred adsorption did not occur as expected, then it would require only one extra test to determine the actual order of preference. Table 3 shows the results of these tests.

The data indicates that $H_2PO_4^-$ and F^- were the two most preferred anions. Hydroxide (OH^-) was not tested as it was assumed that it was the most preferred anion. Tests 3 and 4 show that As(V) is preferred over Se(IV), but is behind fluoride in the series. It appears as though Se(VI) is removed approximately the same in all of the tests with HCO_3^-, SO_4^{2-}, Cl^-, NO_3^-, and H_3AsO_3. In the nitrate-selenate test, very little nitrate is removed and more selenate is adsorbed than nitrate. Therefore, we can assume that Se(VI) is preferred over NO_3. With the arsenite-selenate tests, more Se(VI) is removed than As(III). Since As(III) is in the unionized form, H_3AsO_3, at pH 6.5, it is not expected to be removed to any great degree. Nitrate was more preferred over arsenite.

The data concerning sulfate, bicarbonate, and chloride is hard to interpret. In each test involving one of these species, more was detected in the treated water than in the stock solutions. Because the detection limits are fairly high for SO_4^{2-} and Cl^-, the increases may be more of a reflection on the poor detection limits than anything else. From this data, it is impossible to develop a ranking between SO_4^{2-}, HCO_3^-, Cl^-, and SeO_4^{2-}. Where SeO_4^{2-} falls in preference between these four species is indeterminate.

Based on these tests, the following incomplete series is proposed: OH^-, $H_2PO_4^-$, F^-, $H_2AsO_4^-$, $HSeO_3^-$, (SO_4^{2-}, SeO_4^{2}, -HCO_3^-, Cl^-), NO_3^-, H_3AsO_3. The anions in parenthesis represent the four species whose direct selectivity is unknown. Kubli suggested that sulfate was preferred over chloride, but that is all we know about the interactions of these ions. H_3AsO_3, being in an unionized state in water at pH's less than nine, will be poorly adsorbed, even less than nitrate.

CAPACITIES OF ACTIVATED ALUMINA

A primary step for determining adsorption capacities of activated alumina for selenium (IV) and (VI) is to conduct batch scale isotherm tests. These are done for three reasons: (1) to give a general idea of how effectively activated alumina will

TABLE 3
RESULTS OF SELECTIVITY SERIES TESTS*

Test No.	Species	Initial Concentration (mg/l)	Final Concentration (mg/l)	% Removal	pH_i	pH_f
1	$H_2PO_4^-$	2.0 (as P)	0.03	99	6.2	6.0
	F^-	0.93	0.30	68		
2	F^-	1.19	0.15	87	6.5	6.4
	$H\ SeO_3^-$	4.6 (as Se(IV))	1.5	67		
3	$H\ SeO_3^-$	4.7	2.5	46	6.3	6.5
	$H_2AsO_4^-$	3.6 (as AS(V))	0.9	75		
4	$H_2AsO_4^-$	3.9	1.0	74	6.3	6.4
	F^-	1.15	0.13	88		
5	$H\ SeO_3^-$	4.7	1.0	79	6.2	6.4
	$SO_4^=$	6.8	8.0	--		
6	$H\ SeO_3^-$	4.75	1.05	78	6.3	6.3
	$H\ CO_3^-$	6.5 (as $CaCO_3$)	7.5	--		
7	$H\ CO_3^-$	4.0	8.0	--	6.2	6.5
	SO_4^-	5.4	6.4	--		

---

*Minimum detection limits for Cl^- = 2.0 mg/l
Minimum detection limits for $SO_4^=$ = 2.0 mg/l
Minimum detection limits for HCO_3^- = 0.5 mg/l (as $CaCO_3$)

TABLE 3
(CONTINUED)

Test No.	Species	Initial Concentration (mg/l)	Final Concentration (mg/l)	% Removal	pH_i	pH_f
8	HCO_3^-	6.7	9.8	--	6.4	6.5
	$SeO_4^=$	4.1 (as Se(VI)	3.5	15		
9	$SO_4^=$	5.5	6.4	--	6.1	6.2
	$SeO_4^=$	4.2	3.4	19		
10	$SeO_4^=$	4.2	3.3	21	6.2	6.3
	Cl^-	2.3	2.5	--		
11	$SeO_4^=$	4.4	3.5	20	6.3	6.5
	NO_3^-	0.9 (as N)	0.85	6		
12	$SeO_4^=$	4.3	3.5	19	6.3	6.3
	H_3AsO_3	3.9 (as AS(III)	3.8	3		
13	H_3AsO_3	3.8	3.6	5	6.4	6.5
	NO_3^-	0.9	0.8	11		
14	H_3AsO_3	4.0	3.7	8	6.4	6.4
	Cl^-	2.5	2.8	--		

---

*Minimum detection limits for Cl^- = 2.0 mg/l
Minimum detection limits for $SO_4^=$ = 2.0 mg/l
Minimum detection limits for HCO_3^- = 0.5 mg/l (as $CaCO_3$)

The anions were all added in conjunction with sodium (Na), except for As(V), (As_2O_5) and NO_3^- (KNO_3).

adsorb different forms of selenium present in water. This relatively short screening procedure can usually show whether it is worthwhile to conduct time-consuming column studies, (2) to predict the maximum quantity of selenium activated alumina will adsorb, and (3) to obtain "ballpark" data to judge whether activated alumina may be an economic way to purify a given raw water. Data from isotherms should allow a rough estimate of the size and cost of contactor units.

Figures 20 and 21 show plots of the logarithms of the two variables frequently calculated in isotherm data; the equilibrium concentration of the contaminant (selenium) and amount of contaminant removed per unit weight of activated alumina. Figure 20 is a comparison of the capacities of activated alumina for selenium (IV) and (VI) without any matrix interferences. Either selenium (IV) or selenium (VI) only were added to deionized water and then contacted with the activated alumina.

The activated alumina was prepared as in previous tests; for adsorption of selenium (IV), H_2SO_4 was used for the acid rinse, and for adsorption of selenium (VI), HCl was used for the acid rinse. The general trend shows that if you projected the straight lines for selenium (IV) and selenium (VI), the "Y"-axis intercept for selenium (IV) would be greater than that for selenium (VI). This would indicate a greater capacity for selenium (IV) adsorption than for selenium (VI) adsorption by activated alumina. Note on the plot of selenium (IV) that the sloped line degenerates into a vertical line with decreasing x/m. This indicates that after a certain equilibrium concentration of selenium (IV) (~3 ppb) was attained, no further removal occurred even by adding more activated alumina. This may be an artifact of the decreased accuracy of the AAS to determine amounts less than 5 ppb, or it may be due to the decreased adsorption capacity at low concentrations.

Figure 21 shows the capacity of activated alumina for removing either selenium (IV) or selenium (VI) from a water containing a synthesized mixture of typical constituents of a well water. The composition of this water is described in Section 6. The resulting capacities are lower than in the test with a deionized water matrix.

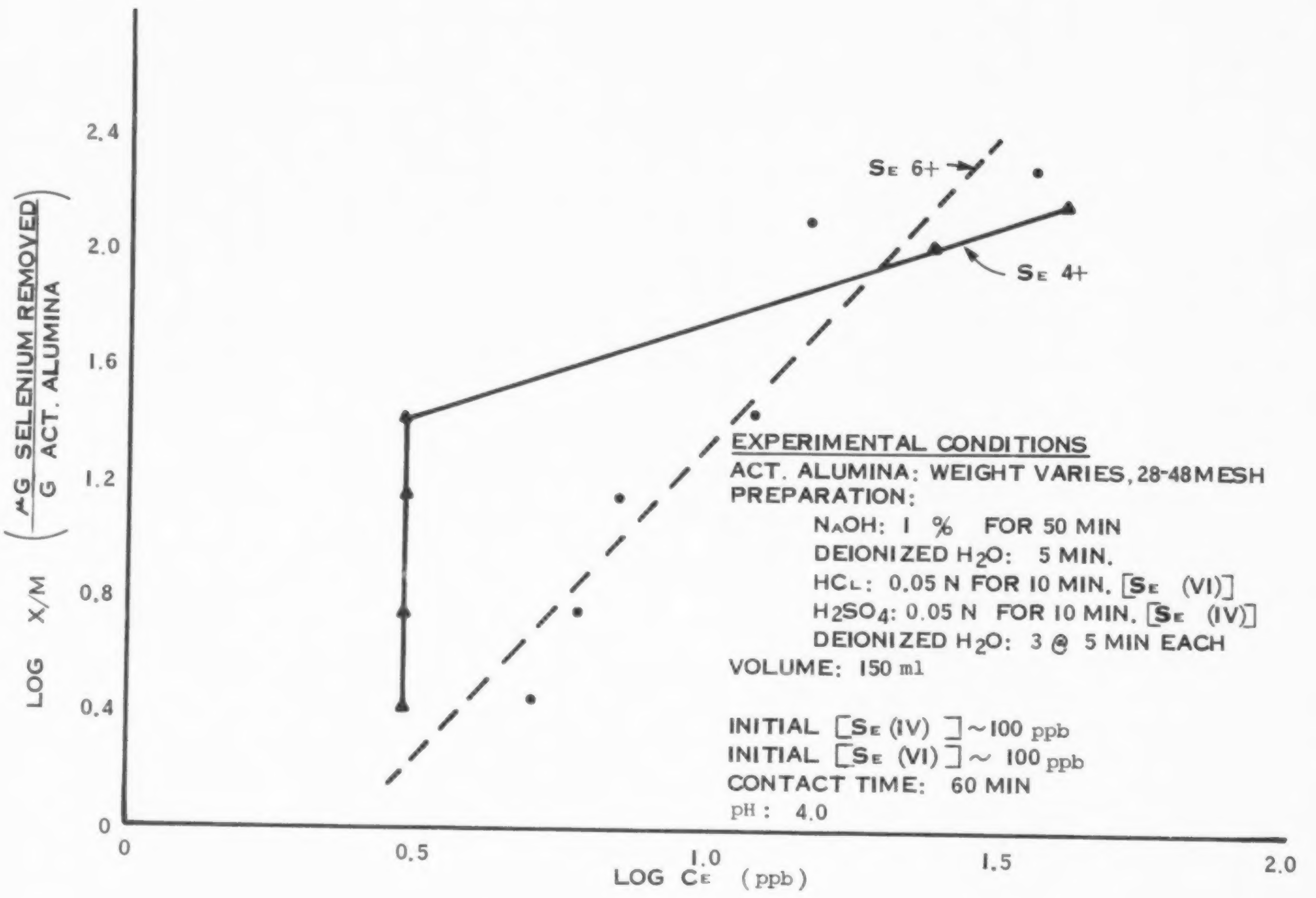


Figure 20. Freundlich isotherm plots of Se (IV) and Se (VI) adsorption in deionized water matrix.

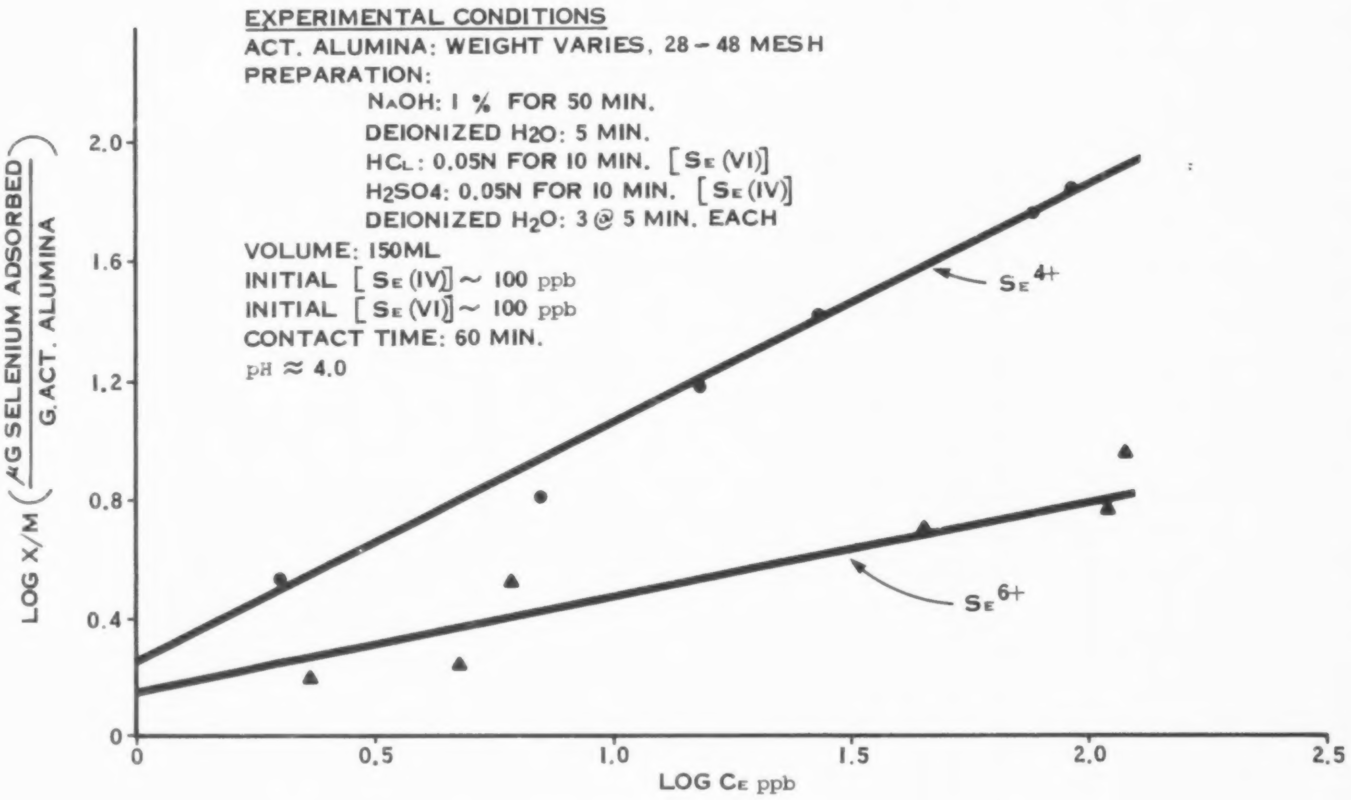


Figure 21. Freundlich isotherm plots of Se (IV) and Se (VI) adsorption in synthesized well water matrix.

Both of the results were approximated by Freundlich isotherms. The adsorption values plotted were calculated according to the Freundlich equation:

$$x/m = K_F C_e^{1/n}$$

or

$$\log x/m = \log K_F + (1/n) \log C_e$$

where x/m = the amount of selenium adsorbed per unit weight of adsorbent (ug/g), C_e = the concentration of selenium in the solution after 1 hour of contact time, and n and K_F are constants. Normally, selenium concentrations and other trace amounts of chemical species in waters are presented as ug/l or ppb. Thus, mass units are more convenient than mole units in the comparison of data, and their use makes no difference in the use of the Freundlich equation except for the constant, K_F:

$$K_F = K_F' \cdot M_W^{(1-n)/n}$$

K_F is on the molar basis, K_F' is on the mass basis, and M_W = the molecular weight of the adsorbate[10].

K_F can be determined from the intercept of the straight line with the "y"-axis. 1/n will be the slope of the straight line. K_F is roughly an indicator of sorption capacity and 1/n of adsorption intensity. As seen in Figure 20 neither of the lines intersects with the "y"-axis. It is shown merely as a comparison with Figure 21. From Figure 21, values of K_F, K_F', and 1/n are tabulated below:

	K_F' (µg/g)	K_F(µmoles/g)	1/n
Se(VI)	1.41	0.069	0.31
Se(IV)	1.66	0.756	0.82

On the basis of the selectivity series, the ions present in the synthesized well water that could be interfering with selenium (IV) and (VI) removal are fluoride, sulfate, and bicarbonate. The presence of $SO_4^=$ and HCO_3^- may cause interferences due to increased adsorption intensity at high concentrations.

Thus, under the same matrix conditions, we can predict the approximate capacity of activated aluminum for selenium from the isotherms. For an initial concentration of 100 ppb and an effluent concentration of 10 ppb (90% removal), approximately 9.5 g of Se(IV) will be removed per gram of activated alumina. Similarly, approximately 3 g of Se(VI) will be removed per gram of activated alumina.

SECTION 6

SELENIUM COLUMN STUDIES

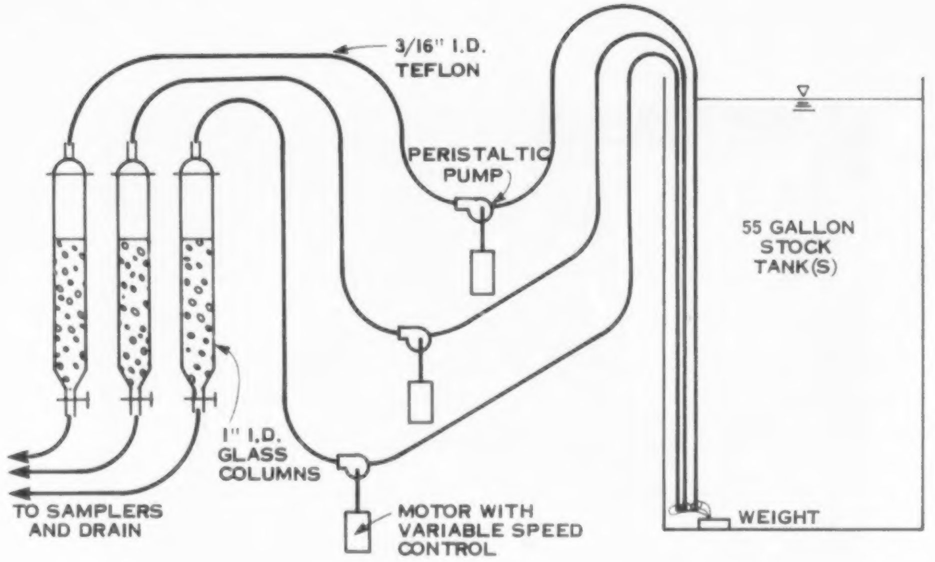
INTRODUCTION

Following the batch tests, continuous flow column studies were initiated to analyze various operating procedures for the use of activated alumina to remove selenium. Figure 22 shows a schematic diagram of the testing equipment. Figure 23 shows a photograph of the actual apparatus. A list of materials and instruments is in the Appendix.

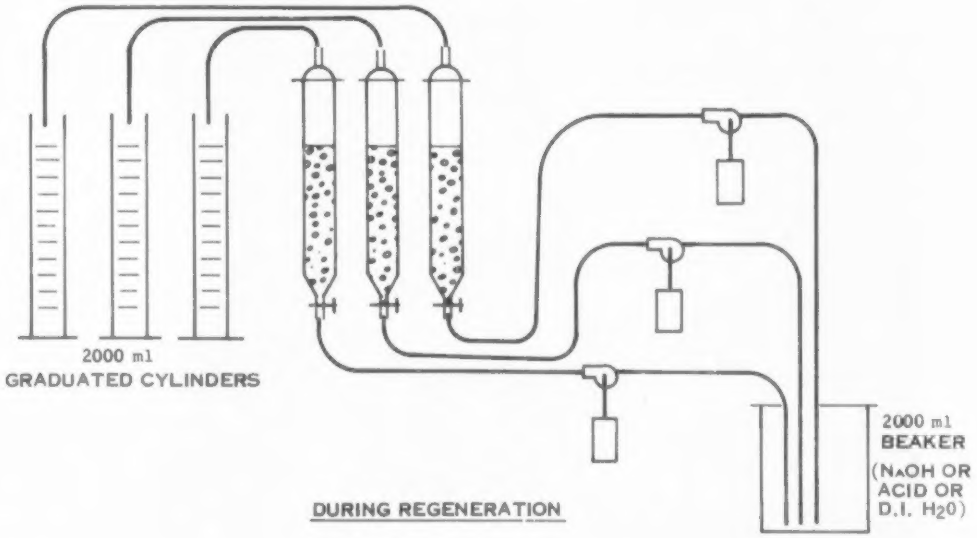
The columns were set up as pressure flow devices. The flow was controlled by the variable speed control (SCR) for the motor. The feed was pulled out of the tank (or tanks) through teflon tubing. The pump tubing was tygon and was connected directly to the teflon tubing on the suction and discharge sides of the pump. Teflon tubing then carried the stock solution into the top of the ground glass joint, which was adapted with Swagelock fittings. At the bottom of the column, above the stop cock, a small amount of fine stainless steel wire mesh was inserted. This was done to prevent alumina from leaking out of the column during regeneration and the subsequent treatment run. Once through the column, the effluent was carried via tygon tubing into a waste trough to drain.

Caustic and acid were mixed in two-liter beakers. Since all the regeneration, neutralization, and rinse steps were done in the upflow mode, the pump connections were merely reversed, with the suction line being fed from either the caustic, acid, or deionized water beaker. The eluants were collected in 2000-ml graduated cylinders to measure the regenerant volumes.

In all of the sample containers, enough concentrated HNO_3 was added as a preservative to keep the pH of the sample < 2. This is an EPA recommended


3/16" I.D. TEFLON
PERISTALTIC PUMP
55 GALLON STOCK TANK(S)
1" I.D. GLASS COLUMNS
TO SAMPLERS AND DRAIN
MOTOR WITH VARIABLE SPEED CONTROL
WEIGHT

DURING REMOVAL RUN


2000 ml GRADUATED CYLINDERS
2000 ml BEAKER
(NaOH OR ACID OR D.I. H2O)

DURING REGENERATION

Figure 22. Schematic diagram of testing equipment during removal run and regeneration. (Not to scale.)

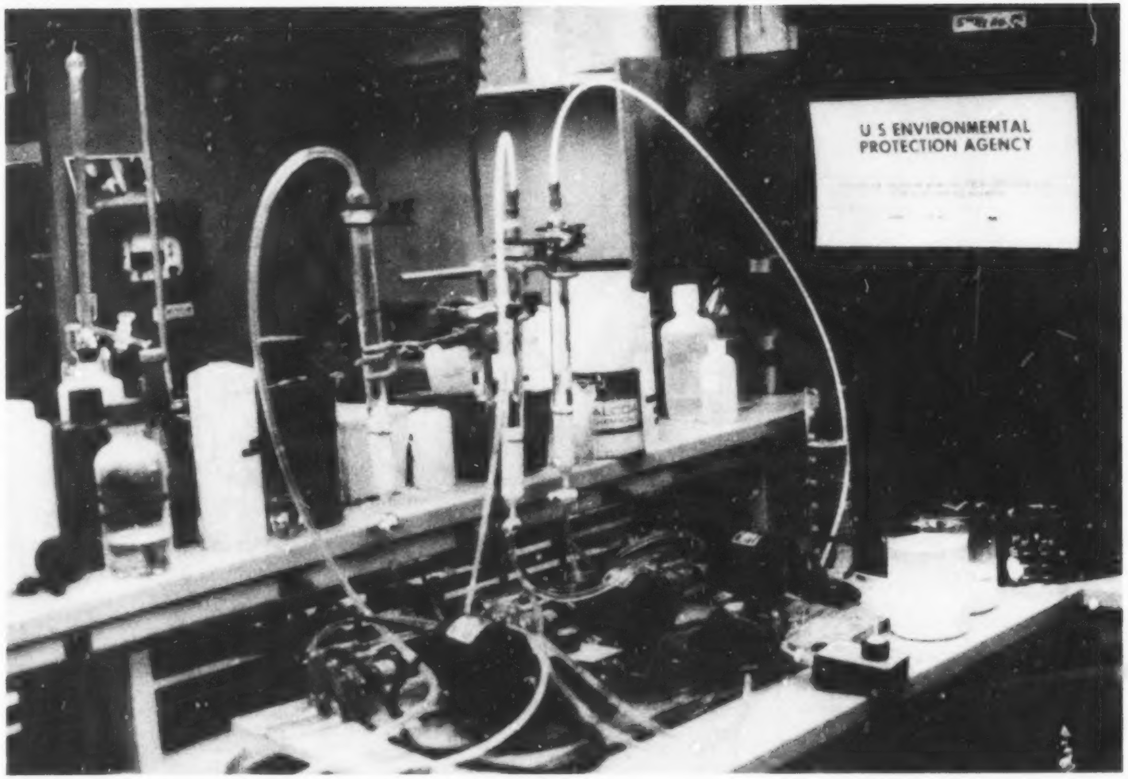

U S ENVIRONMENTAL
PROTECTION AGENCY

Figure 23. Column testing equipment.

preservation method. Even in the regenerant samples with a high pH due to large volumes of NaOH, not enough HNO_3 was added to significantly dilute the sample.

INITIAL TESTING

It was decided to test the ability of activated alumina to remove Se(IV) from deionized water. Three different depths of alumina (3, 6, and 9 inches) were chosen to run side-by-side as a means of comparing the effect of residence time on Se(IV) removal. The respective empty bed contact times were .62, 1.25, and 1.87 minutes. 34, 68, and 102 grams, respectively, of activated alumina were added to achieve those depths.

When preparing fresh out-of-the-can (virgin) activated alumina, the following steps were followed. The alumina was added to a column partially filled with water to prevent solidification of the material. The alumina was then backwashed at a high enough rate (22.0 - 24.5 $\frac{\text{meters}}{\text{hr.}}$ = 9-10 gpm/ft^2) to expand the bed and rinse most of the fines out of the column. Complete regeneration of the virgin media was not required. An initial acid rinse and subsequent deionized (D.I.) water rinse were used.

The removal run with deionized water after the acid rinse showed that no Se(IV) appeared in the effluent after 6,200 bed volumes in the three-inch column and after 3,600 bed volumes and 2,000 bed volumes in the six-inch and nine-inch columns, respectively. This was done at a loading rate of 3 gpm/ft^2 (= 62 ml/min) and a Se(IV) stock concentration of 45 ppb. It was decided that no useful breakthrough data could be obtained from this information, so a synthetic well water was used to effectively model a real-life situation. Previously, work had been done for the Ramona Municipal Water District (RMWD) in San Diego County to evaluate their problem of selenium contamination of a few wells and a synthetic water was prepared to match this quality. Table 4 lists the average composition of the major components of those well waters.

In order to match this quality, a combination of reagents had to be mixed with D.I. water. Table 5 shows the different amounts of these chemicals added to 200 liters of water to achieve the above concentration. The amounts for Se(IV) and Se(VI) are for 0.050 mg/l.

TABLE 4

AVERAGE RMWD WELL WATER COMPOSITION

Species	Concentration (mg/l)
Sodium	145
Potassium	3.0
Calcium	90
Magnesium	40
Bicarbonate Alkalinity	335(as $CaCO_3$)
Sulfate	105
Chloride	230
Nitrate	20
Fluoride	0.90
Selenium	0.005-0.050

TABLE 5

AMOUNTS OF VARIOUS REAGENTS ADDED TO MAKE UP SYNTHESIZED WELL WATER

Reagent	Weight Added (grams)
$CaCl_2$	50.0
$MgCl_2$ $6H_2O$	67.0
$NaHCO_3$	113.0
KF $2H_2O$	0.9
Na_2SO_4	31.0
KNO_3	13.0
Na_2SeO_3 (Se(IV))	0.022
Na_2SeO_4 (Se(VI))	0.024

Freshly mixed, the synthetic solution had a pH of about 8.3. Most of the runs were done at either pH 5, 6, or 7. Based on the batch tests, Cl^- interfered much less than $SO_4^=$ in removal of Se(VI) by activated alumina, hence concentrated HCl was used to adjust the pH instead of H_2SO_4. An analysis was made of the various stock solutions to determine the change in alkalinity and chloride after reducing the pH. The results were:

	Alkalinity (mg/l as $CaCO_3$)	Cl^- (mg/l)
pH 5	22.8	402.6
pH 6	90.6	359.5
pH 7	200.0	312.4

Except for varied amounts of selenium added, these were the only variables in the Se(IV) stock solution during the testing program. In the Se(VI) tests, the matrix remained the same, except for the tests on alkalinity and sulfate interferences.

EXPERIMENTAL SUMMARY

The remainder of this chapter will be a chronological description of each of the column experiments that were conducted during this study. Table 6 provides a summary of each of the experiments along with its objectives and findings so that the reader may easily develop an overall perspective. This table will also serve as an effective reference once the reader has reviewed the ensuing discussion.

CHRONOLOGICAL SUMMARY OF Se(IV) REMOVAL TESTS USING 3-INCH COLUMNS

The data presented in this phase of the column studies does not draw any conclusions as to Se(IV) capacity nor does it define optimum regeneration techniques to efficiently recover Se(IV). The three-inch tests helped to delimit the range of amounts of NaOH and H_2SO_4 in a fairly short period of time. The suggested techniques were then tried with nine-inch deep alumina beds to verify results and optimize operating parameters. The reader may wish to skim through this section to get a general feeling about the process.

TABLE 6

SUMMARY OF RESULTS

Experiment	Objective	Result
SELENIUM (IV) - 3 INCH COLUMN		
1. Effect of contact Time	Determine minimum depth	Use 3-inch bed
2-4. Repeatability tests	Verify 3" depth	3 runs were reproducible
5-6. Regeneration tests: 16, 40, 80 bed volumes of 1% NaOH	Determine amount of NaOH	No apparent difference, leakage increased
7-9. Fresh media - Repeatability runs	Start over - prepare to test regeneration	16 bed volumes of 1% NaOH worked
10. Regeneration tests: 1.6, 16, 80 bed volumes of 0.5% NaOH	Determine amount of NaOH	Lower amount seemed most promising
11-12. Regeneration tests: 1.6, 3.2, 4.8 bed volumes of 0.5% NaOH (#1)	Fine tune NaOH requirement	Too rapid breakthrough-reduce stock feed flow rate to 3 gpm/ft^2
13-14. Regeneration tests: 1.6, 3.2, 4.8 bed volumes of 0.5% NaOH (#2)	Fine tune NaOH requirement	Use 4.8 bed volume of 0.5% NaOH
15-17. Regeneration tests: 0.5%, 1.0%, 2.0% NaOH	Test alumina degradation, selenium (IV) recovery	Higher concentrations dissolved media more, didn't improve regeneration
18-19. Regeneration tests: 1.6, 3.2, 4.8 bed volumes of 0.25% H_2SO_4	Determine optimum H_2SO_4 amount	Use 4.8 bed volumes of 0.25% H_2SO_4
20-22. Regeneration tests: 0.25%, 0.50%, 1% H_2SO_4	Test alumina degradation	Higher concentrations of acid dissolved media faster

TABLE 6

SUMMARY OF RESULTS
(CONTINUED)

Experiment	Objective	Result
SELENIUM (IV) - 9 INCH COLUMN		
1-3. Capacity tests: pH 5, 7.9	Determine optimum pH of stock	pH 5 best, pH 9 forms $CaCO_3$
4. Capacity test: pH 5, 6, 7	Determine optimum pH of stock	pH 5 best, leakage increased, must increase stock concentration
5-6. Capacity tests: C_i - 100 ppb, 1 gpm/ft^2 NaOH	Try to speed up rapid breakthrough and recover 100% of selenium	Must increase stock concentration again
7-12 Capacity tests: C_i = 200 ppb, 1 gpm/ft^2 NaOH	Try to speed up rapid breakthrough and recover 100% of selenium	Regeneration recovers 30-40%, reduce regeneration rate
13-14. Capacity tests: C_i = 200 ppb, 1/2 gpm/ft^2 NaOH	Try to speed up rapid breakthrough and recover 100% of selenium	Recovery 80%
15. Saturation test: C_i = 18 ppm	Saturate media with Se(IV)	Achieved total breakthrough, recovered 80-100%
16-18. Capacity tests: C = 200 ppb, 1/2 gpm/ft^2 NaOH	Try to achieve steady state, evaluate "worst case" capacities	Steady state not achieved, capacity: pH 5 - 235 mg/liter pH 6 - 175 mg/l pH 7 - 100 mg/l
SELENIUM (VI)		
1. 3-inch column	Determine approximate breakthrough	Bed too shallow, use 9-inches
2-3. Repeatability tests	Verify 9-inch depth	Reproducible runs, must reduce NaOH amount
4-5. Regeneration tests: 0.5, 5.3, 53.0 bed volumes of 1% NaOH	Determine amount of NaOH	0.5 bed volumes of 1% NaOH worked as well as 53

TABLE 6

SUMMARY OF RESULTS
(CONTINUED)

Experiment	Objective	Result
SELENIUM (VI) (Continued)		
6-8. Regeneration tests: H_2SO_4 vs. HCl	Determine if H_2SO_4 rinse interferes with Se(VI) removal	Use HCl rinse, H_2SO_4 interferes
9. Regeneration test: pH 5, 7	Determine optimum pH	pH 5 best, 1 gpm/ft^2 NaOH recovered 100% of Se(VI)
10-11. Regeneration tests: 1/2 gpm/ft^2 NaOH	Effect of slower regeneration on recovery of Se(VI)	No increased recovery versus 1 gpm/ft^2
12-13. Regeneration tests: 2 gpm/ft^2 NaOH	Effect of faster regeneration on recovery of Se(VI)	No decreased recovery vs 1 gpm/ft^2
14. Capacity test: pH 5,7	Run another cycle, verify previous results	Approximate capacity: pH 5 - 4.5 mg/liter pH - 1.5 mg/liter
15-16. Sulfate interference	Determine effect of $SO_4^=$ concentration on Se(VI) capacity	$SO_4^=$ heavily interferes, greater capacity with reduced sulfate
17-18. Alkalinity interference	Determine effect of HCO_3^- concentration on Se(VI) capacity	Not as interfering as $SO_4^=$, slight improvement with reduced HCO_3

After terminating the first try at selenium removal in a deionized water matrix, the 3 inch, 6 inch, and 9 inch columns were all regenerated as follows:

20 bed volumes of D.I. water at 9 gpm/ft^2, upflow
80 bed volumes of 1 percent NaOH at 3 gpm/ft^2, upflow
20 bed volumes of D.I. water at 6 gpm/ft^2, upflow
20 bed volumes of 0.05N H_2SO_4 at 3 gpm/ft^2, upflow
20 bed volumes of D.I. water at 6 gpm/ft^2, upflow

A liberal amount of NaOH was used to ensure optimum recoveries of selenium removed during the previous run. Comparisons of Se(IV) removed during a run versus Se(IV) recovered in the regenerant were not conducted until after run 6.

Run No. 1: Effect of Contact Time

Run 1 was done under operating conditions similar to the initial removal run, except that the synthesized well water was used and pH was adjusted to 6.5. As is seen in Figure 24, the three-inch column produced water with less than 10 ppb Se(IV) for 600 bed volumes, the six-inch column produced 750 bed volumes, and the nine-inch column produced 1,100 bed volumes. Due to the length of the exhaustion cycle, operation was not continuous. Later on automatic samplers were used so that breakthrough curves could be monitored through the night. In run 1, two overnight shutdowns were required. The results of this can be seen most dramatically in the three-inch column data. The discontinuities were just after 1,000 and 2,150 bed volumes. Upon restarting in the morning, the effluent concentration markedly decreased from the night before, and thereafter, the slope of the original breakthrough curve was resumed. This would suggest that the adsorption process is "slow" and may be diffusion limited. Notice also that there seem to be plateaus in effluent concentrations. Refer to the discussion after runs 13 and 14 of the Se(IV) nine-inch column experiments for a more detailed explanation of this phenomena.

On the basis of these tests, three-inch columns were chosen to do some preliminary testing regarding various parameters of interest. The presupposition was that the length of a three-inch column run would be six to seven hours, whereas a

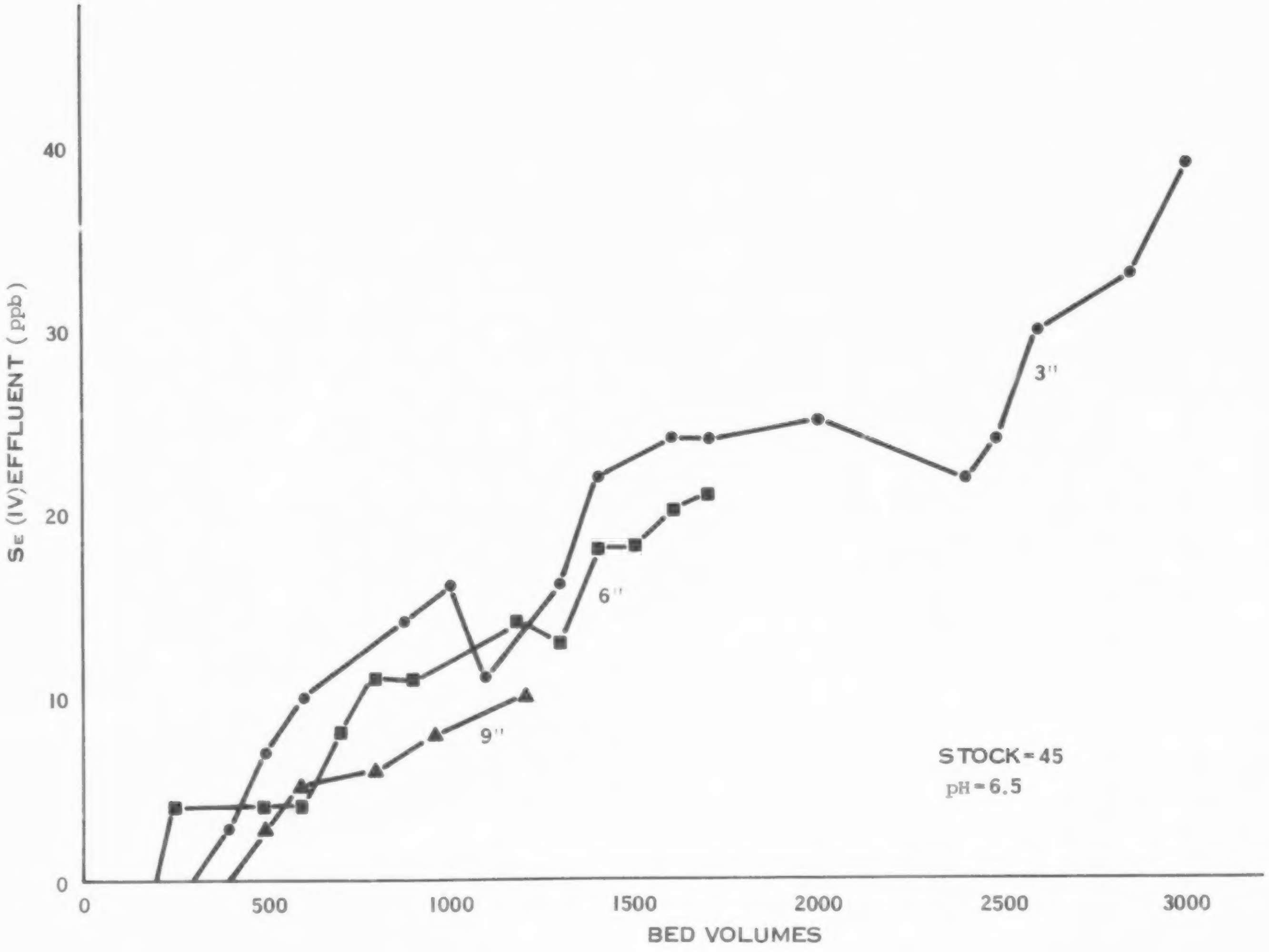


Figure 24. Run 1 -Effect of contact time on Se(IV) removal.

nine-inch run would last about 30 hours. Also, the three-inch columns seemed to provide enough contact time to achieve quality goals at the beginning of the run. Information pertaining to amount and concentration of NaOH, rate at which NaOH is applied, amount and concentration of H_2SO_4, rate at which H_2SO_4 is applied and degradation of the activated alumina by various amounts and concentrations of NaOH and H_2SO_4 can be quickly determined using these short columns. Understandably, capacity information that is generated should not be taken as complete in light of the fact that the deeper columns were able to produce acceptable water for more bed volumes. For all subsequent tests, the removal run was completed during the day, the columns were regenerated, and then sat overnight until the following removal run was started the next morning.

Run Nos. 2-4: Repeatability Tests

Figure 25 shows these runs. The media from the three columns of run 1 was mixed together and three inches were put into each column. Prior to each run, the columns were regenerated as described before run 1. The operating pH was 6.5.

The breakthrough curve for each run is actually a composite of the three columns' data. Since the three columns' effluent qualities were practically identical, the data was averaged and the resultant graph was plotted.

From these tests, it appeared that the three columns would produce long enough runs of high quality water to continue testing with them. The overall removal was still as good as seen in the three-inch column from run 1. A slight decrease in removal was noted from run 3 to run 4.

Runs Nos. 5 and 6: Regeneration Tests, Varied Amounts of NaOH

These runs were done to test the effects of large differences in volume of 1% NaOH in the regeneration. The remaining steps in the regeneration were kept the same. The surface loading rate was increased to 6 gpm/ft^2 because the preceding runs lasted on the order of 10 to 12 hours and we wished to decrease the duration of the runs to six or seven hours. At a stock pH of 6.2, run 5 shows a definite difference

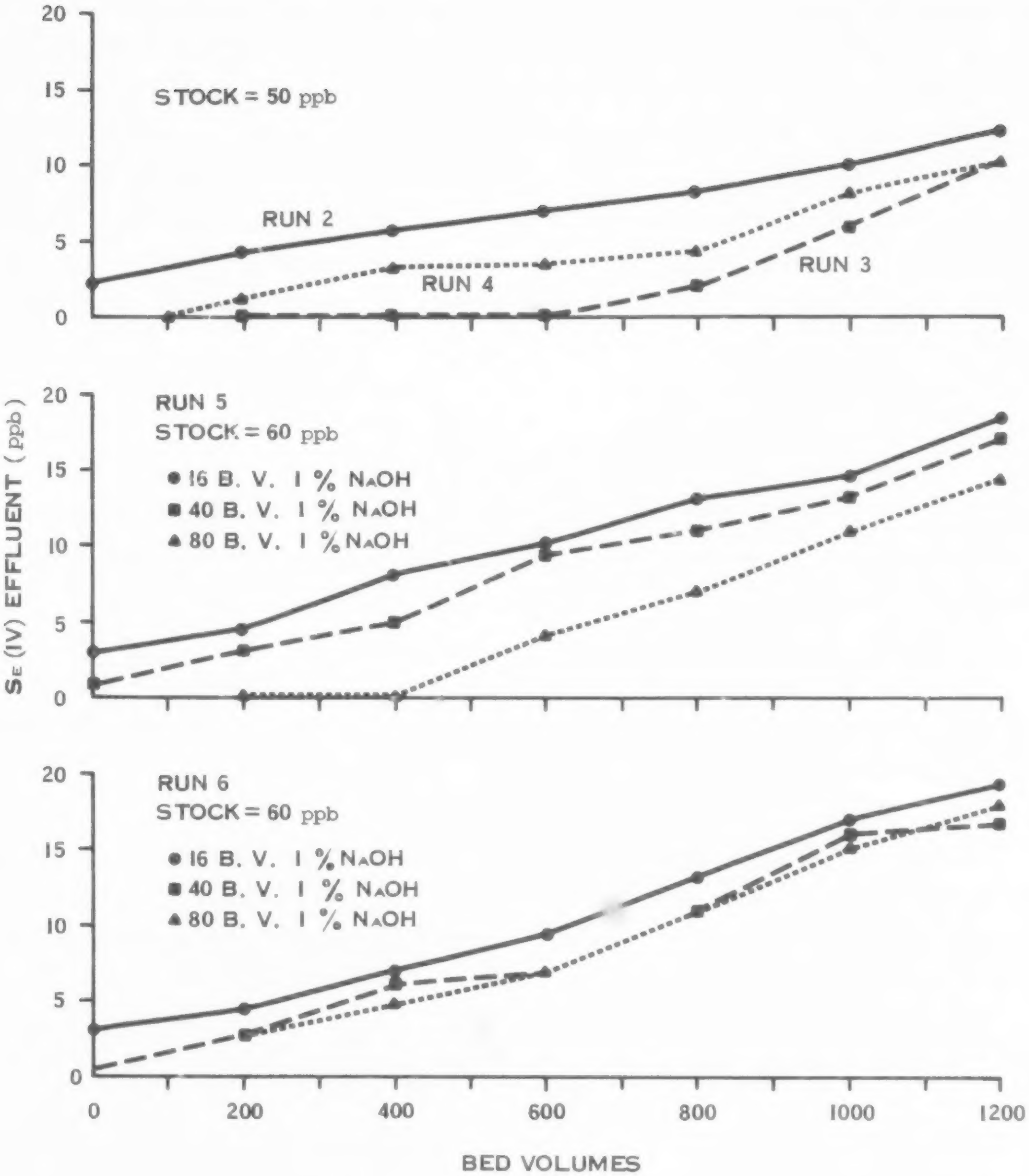


Figure 25. Runs 2 - 6, Regeneration Tests.

between the three columns. The leakages, defined as the amount of Se(IV) present in the column effluent immediately upon the start of a removal run, were 3, 2, and 0 ppb for columns 1, 2, and 3. 600, 800, and 1,000 bed volumes of treated water were produced with a concentration less than 0.010 mg/l. After another similar regeneration, run 6 failed to show the same difference. Figure 25 shows that the effluent concentrations for run 6 were much closer to each other, all having an initial leakage of 2 or 3 ppb and 700-800 bed volumes until a 0.010 mg/l breakthrough occurred.

Run Nos. 7-9: Fresh Media, Repeatability Runs

After run 6, it was decided to remove the old media and start with a fresh batch. Because the history of each column varied quite a bit, it was difficult to predict how each compared with the others. A main point that should be brought out here is that the process shows a lot of hysteresis and the history of each bed's exhaustion and regeneration plays an important role in determining how it will operate in a removal run. Inefficient regeneration in one column and not the others will allow more selenium to remain on the alumina, thus diminishing its capacity for removal. Even in side-be-side comparisons, this may lead to inaccurate conclusions.

Although experiments 2 through 6 develop useful data on relative performance, they also demonstrated that the experimental conditions used did not result in reproducible data and did not allow reasonable projections of adsorption capacity. As a result, several changes were made in the operating conditions to match them to conditions shown earlier to be suitable for fluoride removal in large scale facilities. These conditions were summarized by Trussell[29] following an extensive review of data from the literature and the field. It was presumed that the nature of the process of adsorption/elution of Se(IV) and Se(VI) on activated alumina did not necessite operating conditions different from fluoride.

Runs 7-9 (Figure 26) represent three consecutive runs done with initially fresh activated alumina in 3-inch columns. Preceding run 7, only a 0.05N H_2SO_4 rinse for 10 bed volumes at 3 gpm/ft^2 followed by 20 bed volumes of D.I. water rinse at 6 gpm/ft^2 was done. Both of these rinses were upflow. Preceding runs 8 and 9, the following regeneration took place:

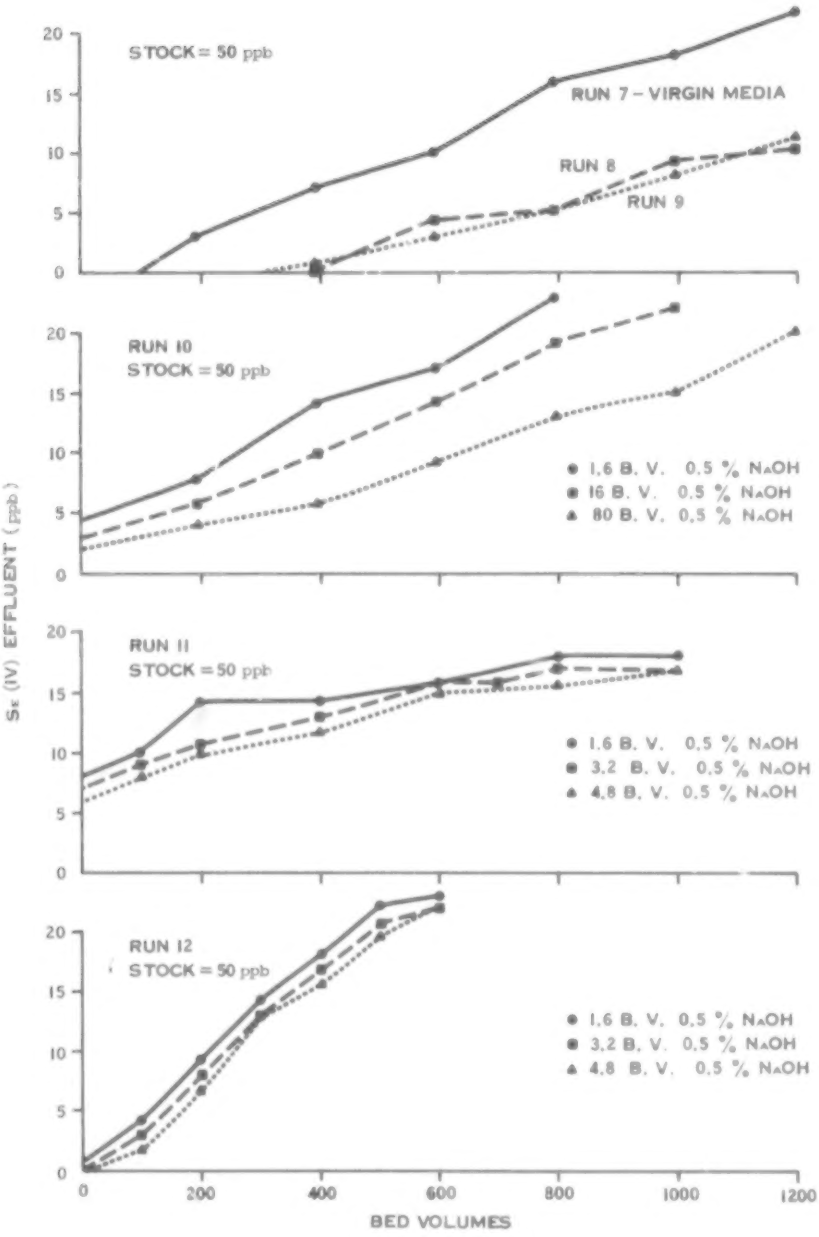


Figure 26. Runs 7 - 12, Regeneration Tests.

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10 bed volumes of D.I. water at 9 gpm/ft^2, up
16 bed volumes of 1 percent NaOH at 3 gpm/ft^2, up
20 bed volumes of D.I. water at 6 gpm/ft^2, up
8 bed volumes of 0.05 H_2SO_4 at 3 gpm/ft^2, up
10 bed volumes of D.I. water at 6 gpm/ft^2, up

The treatment run was operated at 6 gpm/ft^2. Seen from the figure, run 7 is much poorer than runs 8 and 9. Again, the runs are composites of the three columns effluent curves for each run. Only slight differences were found between any of the columns in any run. 8 and 9 show a breakthrough capacity of 1,100 bed volumes. The following chart shows the amounts of Se(IV) removed during the run and recovered during the following regeneration. Calculation of the removal during the run was done by integrating the area above the breakthrough curve using the stock concentration of 65 ppb. Regenerant amounts were determined by knowing the volume of regenerant and analyzing the regenerant for Se(IV).

Run	Se(IV) Removed During Run (mg)	Se(IV) Recovered During Subsequent Regeneration (mg)	% Recovery
7	2.87	1.50	52
8	3.25	1.48	46
9	3.20	--	--

Approximately 50 percent of the selenium removed is recovered by the regeneration. If continued like this for many repetitive cycles, the percent recovery should approach 100 as the Se(IV) removed during each run grows progressively less.

Run No. 10: Regeneration Test, Varied Amounts of NaOH (#1)

Following run 9, it was decided to test various amounts of 0.5 percent NaOH on the three columns. 0.5% NaOH was chosen because a review of the current operating procedure at a full-scale fluoride removal facility used this concentration. It was assumed that each column had undergone the same history since using the virgin alumina in run 7. Column 1 was given 1.6 bed volumes of 0.5 percent NaOH at 3 gpm/ft^2, upflow, and Columns 2 and 3 were given 16 and 80 bed volumes, respectively at the same concentration and rate. Recoveries were as follows in mg:

Column 1 - 0.32 = 10 percent recovery
Column 2 - 1.82 = 57 percent recovery
Column 3 - 2.4 = 75 percent recovery

As Figure 26 depicts, run 10 at a surface loading rate 6 gpm/ft^2 showed obvious differences. The leakage for columns 1, 2, and 3 was 4, 3, and 2 ppb respectively. Removals of Se(IV) during the run were 1.48 mg, 1.72 mg, and 1.86 mg with breakthrough occurring at 250, 400, and 650 bed volumes. In looking at the removals of Se(IV) during regeneration, column 2 used ten times as much regenerant as column 1, but recovered only six times as much selenium. Column 3 used fifty times as much regenerant, but recovered only 7.5 times as much selenium. This fact led us to believe that the optimum recovery of Se(IV) would fall in the range of 1.6 to 16 bed volumes of 0.5 percent NaOH, with a better chance of the range being 1.6 to 8 bed volumes. Hence, runs 11 and 12 were done with 1.6, 3.2, and 4.8 bed volumes of 0.5 percent NaOH at 3 gpm/ft^2 as the regenerant. The other steps in the regeneration remained the same as described in run 7.

Runs Nos. 11-12: Regeneration Tests: Small Amounts of NaOH

Figure 26 shows runs 11 and 12. Run 11 shows leakage in the range of 6 to 8 ppb and a very rapid breakthrough to 10 ppb. Run 12 had leakage from 0 to 1 ppb and the change from the previous run is probably due to lesser amounts of selenium present to be regenerated. However, the slope of the breakthrough curve increased rapidly, resulting in a very sharp decrease in adsorption capacity. Table 7 shows the removals and recoveries for the two runs.

As a matter of reference, 1.6, 3.2, and 4.8 bed volumes of 0.5% NaOH correspond to the following doses, respectively:

$$8.0,\ 16.0,\ \text{and}\ 24.0\ \frac{\text{grams NaOH}}{\text{liter act. alumina}} = 0.5,\ 1.0,\ 1.5\ \text{lb/ft}^3$$

Pounds of regenerant per cubic foot of bed and grams per liter are typical ways to discuss regerant doses in ion exchange literature.

TABLE 7

REMOVALS AND RECOVERIES OF Se(IV) FOR RUNS 10, 11, AND 12

Run	Se(IV) Removed During Run (mg)	Se(IV) Recovered in Subsequent Regeneration (mg)	Amount of 0.5% NaOH Used (Bed Volumes)	% Recovery
10	1.48	0.15	1.6	10
	1.72	0.20	3.2	12
	1.86	0.27	4.8	15
11	1.36	0.15	1.6	11
	1.41	0.19	3.2	13
	1.44	0.25	4.8	17
12	1.05	--	--	--
	1.21	--	--	--
	1.18	--	--	--

Run Nos. 13-14: Regeneration Tests, Smaller Amounts of NaOH (#2)

Due to the relatively poor breakthrough capacity exhibited by the previous runs, an adjustment had to be made. The empty bed residence time in the activated alumina during the previous runs was 0.31 minute (38.7 ml/124 ml/min.). This was determined to be too short. This prompted us to return to a lower surface loading rate of 3 gpm/ft^2 (= 7.3 meters/hour). This doubled the previous residence time and hopefully would show more promising results.

Runs 13 and 14 were conducted under the same regenerative scheme as runs 11 and 12, the only difference being the treatment rate of 3 gpm/ft^2. Figure 27 shows leakage was less than the other two runs and that the breakthrough capacity increased to 600-700 bed bolumes for run 13, but dropped to 300-400 bed volumes for run 14. It is evident that the larger the amount of 0.5 percent NaOH used, the less leakage and a greater capacity in the following runs were produced. Table 8 shows recoveries and removals for runs 12, 13, and 14.

Because of the results of runs 13 and 14, 4.8 bed volumes of 0.5 percent NaOH at 3 gpm/ft^2 was adopted as the regenerant dose. This is equivalent to 24.0 g/l or 1.5 #/ft^3.

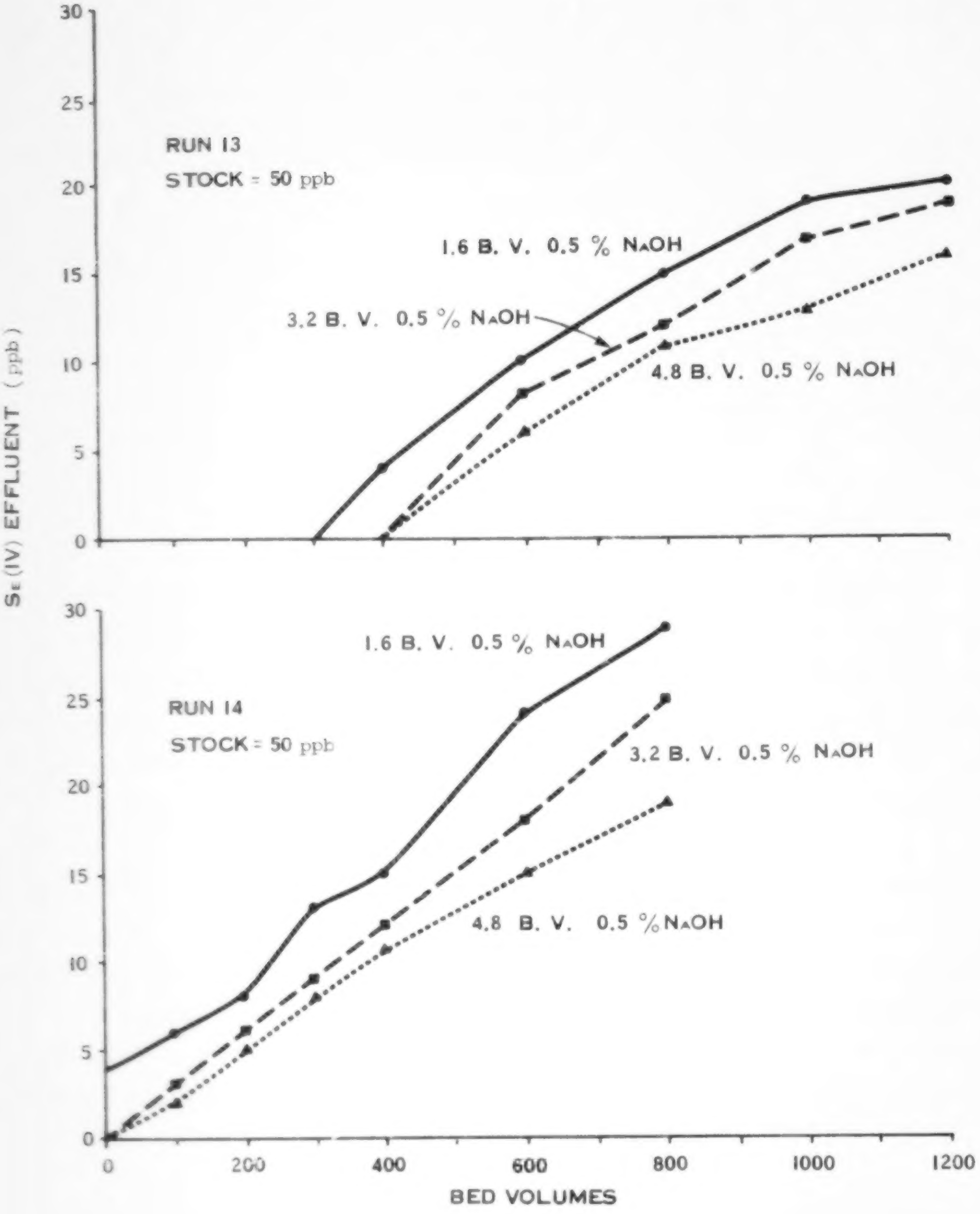


Figure 27. Runs 13 and 14, Regeneration Tests.

TABLE 8

REMOVALS AND RECOVERIES OF Se(IV) FOR RUNS 12, 13, AND 14

Run	Se(IV) Removed During Run (mg)	Se(IV) Recovered in Subsequent Regeneration (mg)	Amount of 0.5% NaOH Used (Bed Volumes)	% Recovery
12	1.05	0.04	1.6	4
	1.21	0.09	3.2	7
	1.18	0.15	4.8	13
13	1.87	0.07	1.6	4
	1.96	0.13	3.2	7
	2.03	0.22	4.8	11
14	1.06	--	--	--
	1.17	--	--	--
	1.24	--	--	--

Runs Nos. 15-17: Regeneration Tests: 0.5%, 1.0%, 2.0% NaOH

Runs 15, 16, and 17 were done with a 1.5 #/ft^3 NaOH dose, but the concentrations were varied to see if they had any bearing on regeneration efficiency or activated alumina degradation. The other regeneration steps were kept the same as in previous runs. For 0.5 percent NaOH, regeneration time was 3 minutes. Respective times for 1.0 percent and 2.0 percent were 1.5 and 0.75 minute. Figure 28 shows virtually no difference in any of the breakthrough curves between the three columns for any given run. The breakthrough capacity for both runs 15 and 16 were 500 bed volumes, while it increased to 800 bed volumes in run 17. This is probably due to the decreased stock concentration of 35 ppb Se(IV) for this run. Table 9 shows removal and recoveries of Se(IV) in runs 14, 15, 16, and 17.

Under these conditions, it appears as though 0.30 mg - 0.35 mg of Se(IV) can be recovered during regeneration. Upon a number of repetitive cycles, this would be expected as the equilibrium amount of Se(IV) that could be removed during a removal run. The difference between the different concentrations of NaOH in recovering Se(IV) is very small.

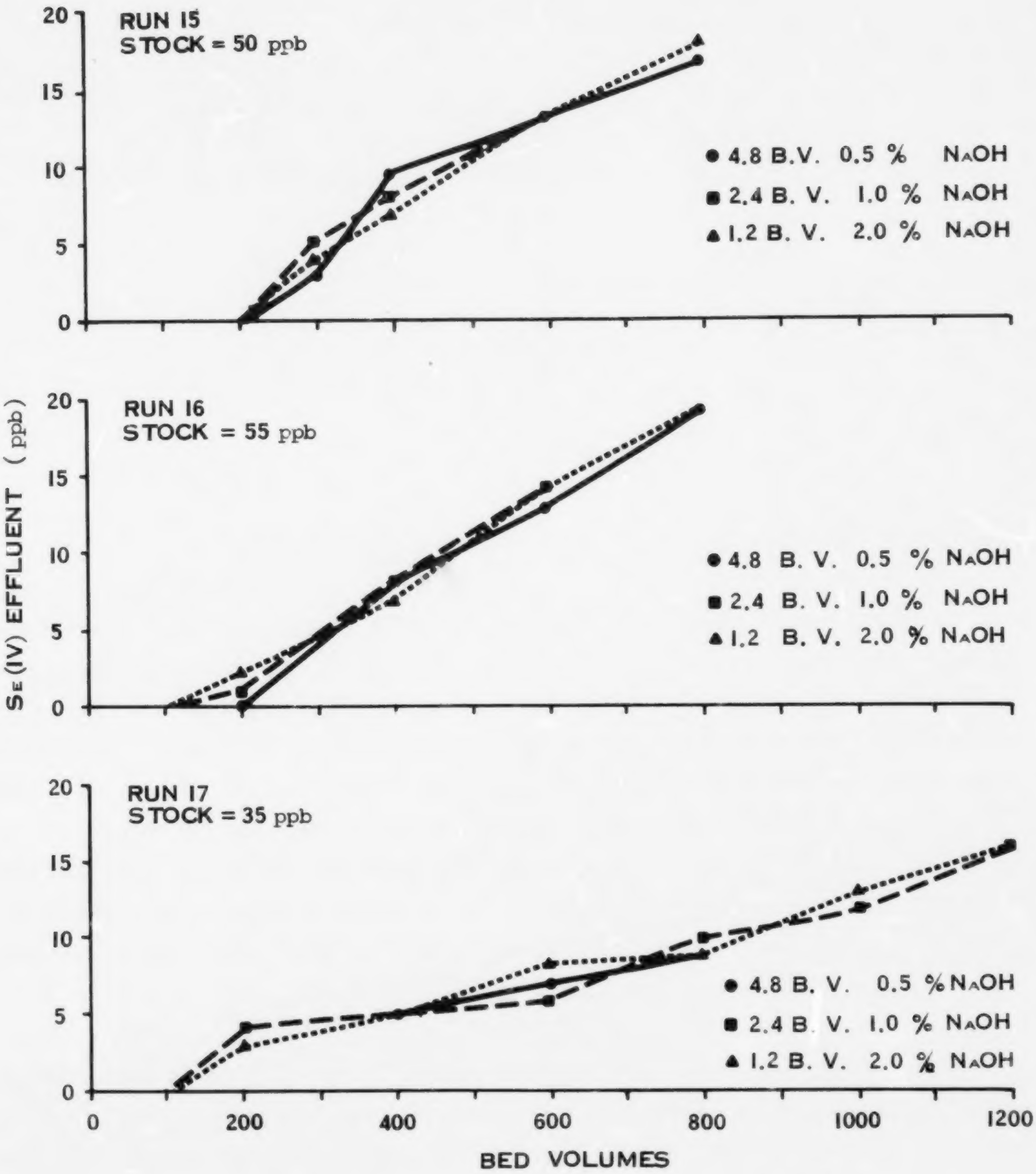


Figure 28. Runs 15 - 17, Regeneration Tests.

Table 9 shows that increasing concentrations of NaOH regenerant have little effect on the ability to remove Se(IV), providing that the dose of NaOH per volume of activated alumina is kept the same. Quite possibly the effect of increasing the driving force for elution (increased concentration) is negated by the decreased flow through time in the bed. If the concentration of NaOH is doubled while keeping the dose the same, it will take only one-half the time to complete this. Actual duration of contact between the NaOH and the activated alumina may be very important in determining optimum regenerative techniques.

TABLE 9

REMOVALS AND RECOVERIES OF Se(IV) FOR RUNS 14, 15, 16, AND 17

Run	Se(IV) Removed During Run (mg)	Se(IV) Recovered in Subsequent Regeneration (mg)	% NaOH	% Recovery
	1.06	0.32	0.5	30
14	1.17	0.33	1.0	28
	1.24	0.34	2.0	27
	1.31	0.32	0.5	24
15	1.31	0.34	1.0	26
	1.32	0.35	2.0	27
	1.47	0.31	0.5	21
16	1.45	0.23	1.0	16
	1.45	0.32	2.0	22
	1.28	--	--	--
17	1.29	--	--	--
	1.28	--	--	--

Table 10 depicts the comparative amounts of aluminum removed during regeneration under the above described conditions, 1.5 #NaOH/ft^3, operating with 0.5 percent, 1.0 percent, and 2.0 percent NaOH. This amount was present in a combined sample containing the initial backwash, the NaOH rinse and the subsequent deionized water rinse. Samples were analyzed for aluminum on the flame AAS and the percent of activated alumina removed was calculated by converting from Al to Al_2O_3.

Table 10 gives an indication that higher concentrations of NaOH were able to dissolve activated alumina faster while keeping the dose the same. This will be verified in future tests. From this data the following numbers of cycles could be completed at each concentration of NaOH before all of the alumina would be dissolved:

0.5% NaOH - 910 cycles
1.0% NaOH - 770 cycles
2.0% NaOH - 625 cycles

TABLE 10

DEGRADATION OF ACTIVATED ALUMINA BY VARIOUS CONCENTRATIONS OF NaOH

Al Recovered in Subsequent Regeneration ((mg)
(% by Weight of 3-inch column in parenthesis)

Run	0.5% NaOH	1.0% NaOH	2.0% NaOH
14	18.6 (0.09%)	21.0 (0.10%)	26.5 (0.13%)
15	24.5 (0.12%)	32.0 (0.16%)	39.3 (0.20%)
16	22.0 (0.11%)	26.8 (0.13%)	32.6 (0.16%)

Operating conditions:

10 bed volumes of D.I. water at 9 gpm/ft^2, up

1.5 $\frac{\#NaOH}{ft^3}$ at 3 gpm/ft^2 w/0.5%, 1.0%, 2.0% NaOH, up

15 bed volumes of D.I. water at 6 gpm/ft^2, up

On another basis, if a column was regenerated once every day, after one year the following percentages of original weight would need to be replaced.

0.5% NaOH - 40%
1.0% NaOH - 47%
2.0% NaOH - 58%

Remember that these figures are only for the dissolution of activated alumina by NaOH. Additional degradation is expected by the acid rinse. The above differences could mean quite a bit of extra money being spent on replacing media on an annual basis. Currently, type F-1, 28-48 mesh is selling for \$0.60/lb. For the above figures, the following annual costs for replacement of media could be expected for an activated alumina contactor with a volume of 250 ft^3, with regeneration every day. This size contactor was taken from a typical fluoride removal facility with a capacity of 0.7 mgd.[28]

0.5% NaOH - \$3,300
1.0% NaOH - \$3,900
2.0% NaOH - \$4,800

Run Nos. 18-19: Regeneration Tests: Varied Amounts of H_2SO_4

The next step was to determine the optimum acid rinse for a given dose of NaOH. The limits set for testing were again taken from a review of operating procedures at a full-scale fluoride removal facility. 1.6, 3.2, and 4.8 bed volumes of 0.05N H_2SO_4 (= 0.25% H_2SO_4) were evaluated on their ability to reduce the pH of the bed and its effect on Se(IV) adsorption. The regeneration prior to the acid rinse was as follows:

10 bed volumes D.I. water at 9 gpm/ft^2, up
4.8 bed volumes of 0.5% NaOH at 3 gpm/ft^2, up
10 bed volumes of D.I. water at 6 gpm/ft^2, up

Figure 29 shows that there is no discernable difference in the breakthrough curves for the different acid rinses. However, the pH of the activated alumina was noted after the final rinse (which consisted of 5 bed volumes of D.I. water at 6 gpm/ft^2). For 1.6 bed volumes of 0.5N H_2SO_4, the pH was 10.0-10.5. For 3.2 bed volumes, the pH was 9.0-9.5, and for 4.8 bed volumes, the pH was 5.5-6.5.

Note that the bed volumes until breakthrough increased from 200 in run 18 to 900-1,000 in run 19. This may be partially due to the change in stock concentration from 60 ppb to 40 ppb.

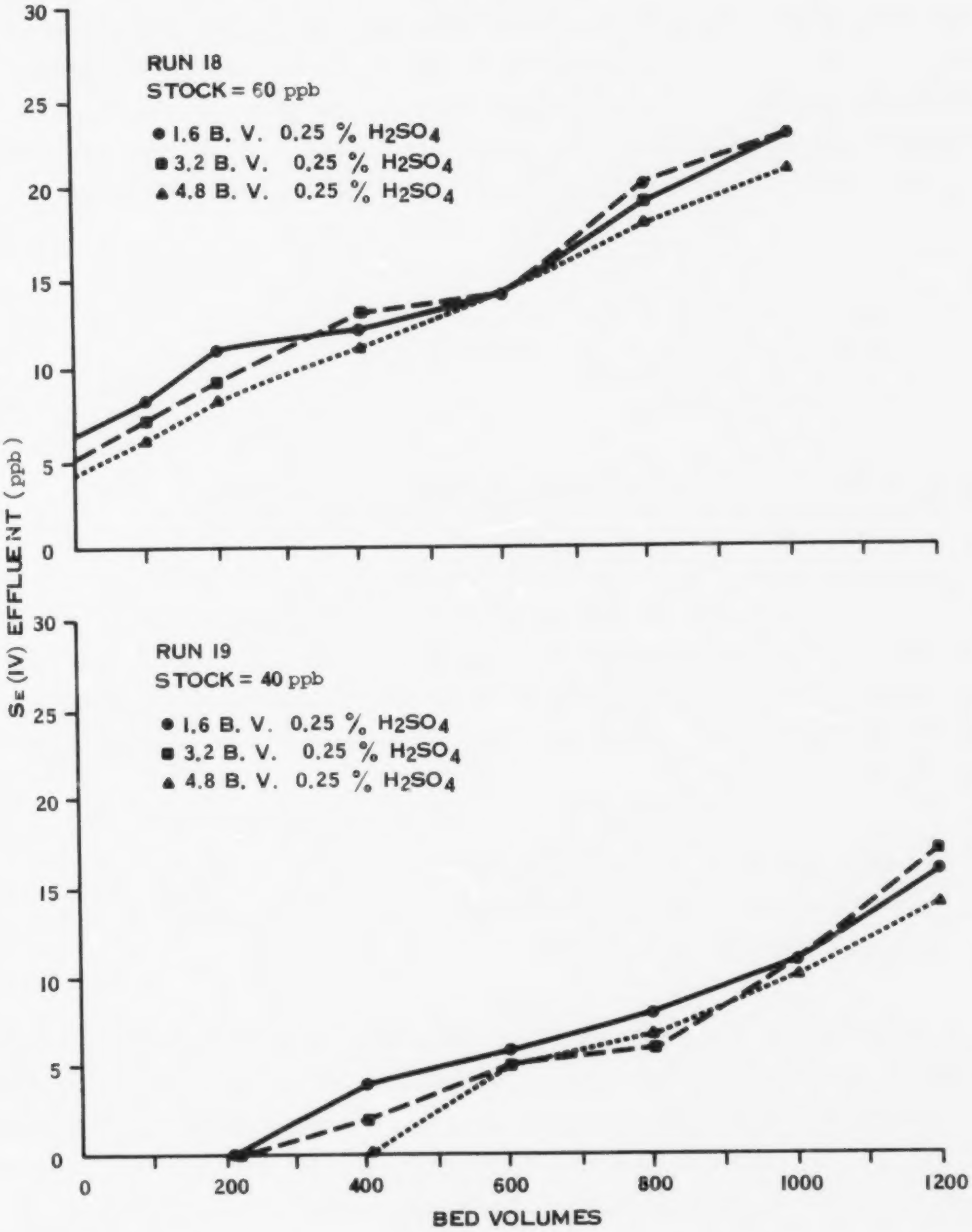


Figure 29. Runs 18 and 19, Regeneration Tests.

Run Nos. 20-22: Regeneration Tests, 0.25%, 0.50%, 1.0% H_2SO_4

From the above data, it was decided to use the equivalent of 4.8 bed volumes of 0.05N H_2SO_4 for the acid rinse. This is a dose of 0.75 #H_2SO_4/ft^3 bed. Runs 20 through 22 are very similar to the varied concentrations of NaOH runs, 15 through 17. Keeping the other regeneration steps constant, 0.75 #/ft^3 H_2SO_4 was applied at 0.05N, 0.10N, 0.20N H_2SO_4 at 3 gpm/ft^2. The amount of time it took to do this was 3.0, 1.5, and 0.75 minutes, respectively. No real difference was expected in the breakthrough curves. Regeneration following runs 19, 20, and 21 was as follows:

10 bed volumes D.I. water at 9 gpm/ft^2, up
4.8 bed volumes of 0.5 percent NaOH at 3 gpm/ft^2, up
10 bed volumes of D.I. water at 6 gpm/ft^2, up
4.8, 2.4, and 1.2 bed volumes of 0.05N, 0.10N, 0.20N H_2SO_4 at 3 gpm/ft^2, up
10 bed volumes of D.I. water at 6 gpm/ft^2, up

Table 11 gives the removals and recoveries of Se(IV) for the NaOH and H_2SO_4 rinses for runs 19 through 22 (Figures 29 and 30). Caustic rinses contained the initial backwashes and intermediate rinses. Acid rinses included the final rinses.

Notice that the acid rinse removed in the range of 7%-13% of the total Se(IV) recovered during regeneration. There should be some removal expected from the acid rinse because it is very concentrated compared to the Se(IV) concentration on or in the alumina, even though Se(IV) is preferred over $SO_4^=$ in the selectivity series.

Figure 30 shows that the bed volumes to breakthrough vary from 200 to 400. The leakage is still significant and reduces the volume capacity until breakthrough.

Table 12 shows the amount of dissolved aluminum present in the acid rinse portion of the regeneration for runs 19 through 21. No regeneration was done after run 22, therefore, no data is available. As before, the aluminum was analyzed by the flame AAS and the present of total weight involved the conversion of Al to Al_2O_3.

Table 12 shows aluminum has a moderately higher solubility in the more concentrated acid. Although the differences aren't that great, there is a trend that

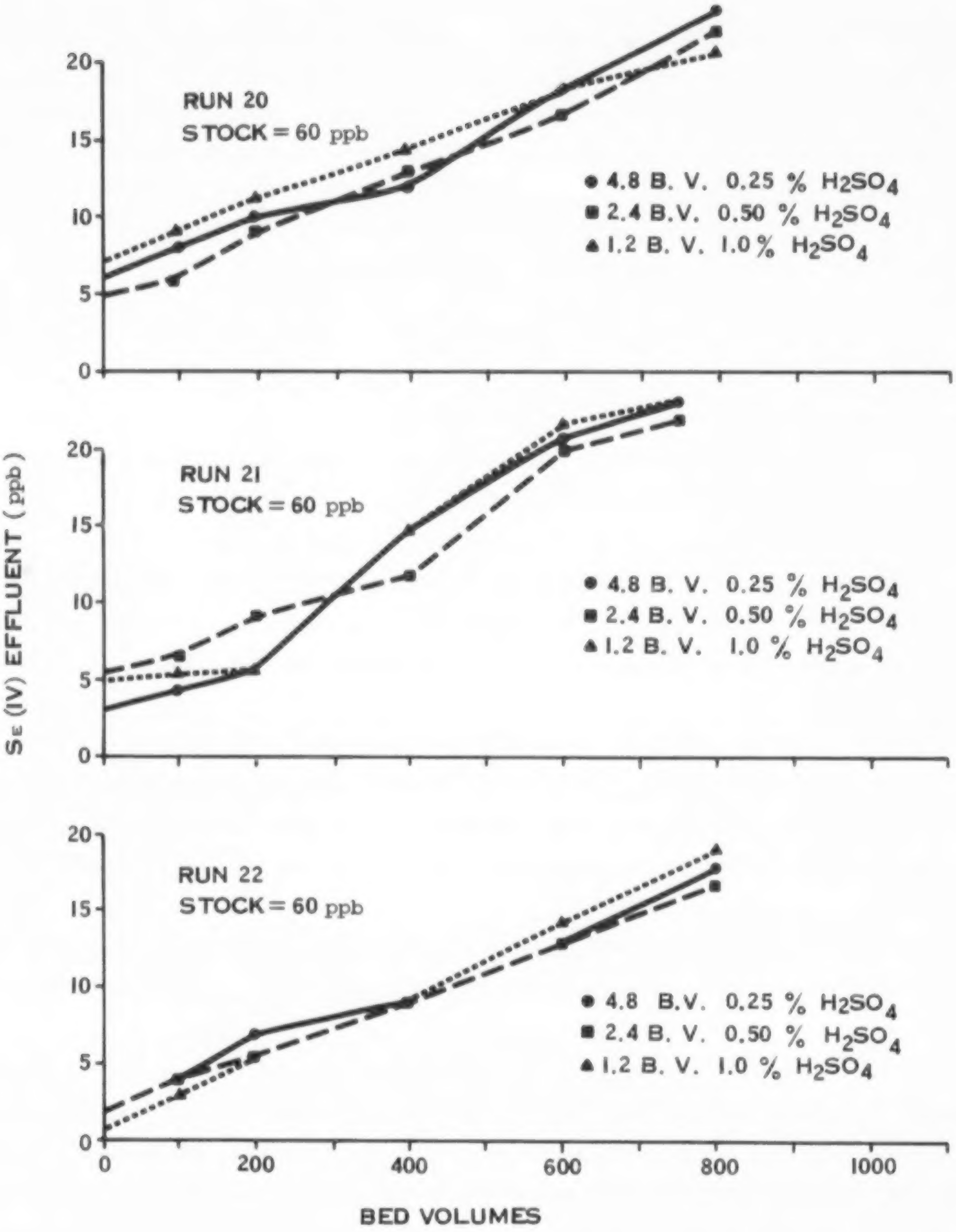


Figure 30. Runs 20 - 22, regeneration tests.

would suggest using a less concentrated acid to prevent rapid dissolution of the alumina. In comparison with Table 10, approximately one-third to one-fourth of the amount removed from the bed during the caustic rinse is removed in the acid rinse. This will be verified in deeper column tests.

TABLE 11

REMOVALS AND RECOVERIES OF Se(IV) FOR NaOH AND H_2SO_4 RINSES DURING RUNS 19, 20, 21, AND 22

Run	Removal of Se(IV) During Run (mg)	Recovery of Se(IV) During Subsequent Regeneration (mg) NaOH	H_2SO_4	Concentration of H_2SO_4 Used	% Total Se(IV) Recovery
19	1.58	0.44	0.035	0.05N (0.25%)	30
	1.59	0.46	0.054	0.10N (0.5%)	32
	1.68	0.44	0.037	0.20N (1.0%)	28
20	1.43	0.42	0.062	0.05N	34
	1.45	0.45	0.070	0.10N	36
	1.42	0.44	0.054	0.20N	35
21	1.42	0.45	0.056	0.05N	36
	1.44	0.43	0.066	0.10N	34
	1.41	0.44	0.041	0.20N	35
22	1.56	--	--	-	--
	1.57	--	--	-	--
	1.56	--	--	-	--

TABLE 12

DEGRADATION OF ACTIVATED ALUMINA BY VARIOUS CONCENTRATIONS OF H_2SO_4

Al Recovered in Subsequent Regeneration (mg)
(% by Weight of 3-inch bed in Parenthesis)

Run	0.25%	0.50%	1.0%
19	5.2 (0.03%)	7.2 (0.04%)	8.9 (0.04%)
20	6.9 (0.03%)	5.2 (0.03%)	10.8 (0.05%)
21	6.1 (0.03%)	7.6 (0.04%)	8.9 (0.04%)

CHRONOLOGICAL SUMMARY OF Se(IV) REMOVAL TESTS USING NINE-INCH COLUMNS

In reviewing the three-inch column data, a couple of key points were noted. When doing countercurrent regeneration (where the direction of regenerant flow is opposite to that of the treatment cycle), it is important to keep the particles of the alumina in the same place during regeneration. The strongest portion of regenerant will react with the least saturated (in terms of Se(IV)) amount of alumina. At the top of the bed, the weakened NaOH will still be able to regenerate the more saturated alumina. In ion exchange processes, co-current regeneration sometimes presents leakage problems, but countercurrent processes minimize leakage and the use of regenerant. Therefore, a high rate backwash prior to the regeneration was excluded from the regeneration program. This backwash mixed the bed thoroughly and altered the distribution of alumina that was present during the treatment run. Also, the rates at which the intermediate and final D.I. rinses were done were lowered. Since those high rates (6 gpm/ft^2) caused some expansion of the bed and mixing, it was thought that reducing the rate would increase the rinsing efficiency.

The majority of the information we hoped to obtain related to the capacity of the activated alumina for Se(IV) under varying conditions of pH and regenerant flow rate. Since these tests with 9-inch columns were expected to last from 36 to 48 hours at a treatment flow rate of 3 gpm/ft^2, and each column was going to be operated at a different pH, each column had to have its own separate tank of stock solution. Slight variations in the synthetic well water composition could occur and the Se(IV) concentration could greatly vary. However, extra care was taken to ensure that each container received the same amounts of each constituent. After the mixing and pH adjustment, the solutions were allowed to sit for 24 hours to ensure that bubbles were removed from the water and did not enter the columns.

Since the 9-inch column runs would last overnight, a method was needed to collect samples during the period when no one was attending the columns. We obtained three automatic samplers, called "Wastewatchers" that took a sample every hour up to 24 hours. See Figure 31 for a photograph of a "Wastewatcher." The effluent drain lines were put into 250 ml beakers in the drain trough and allowed to fill

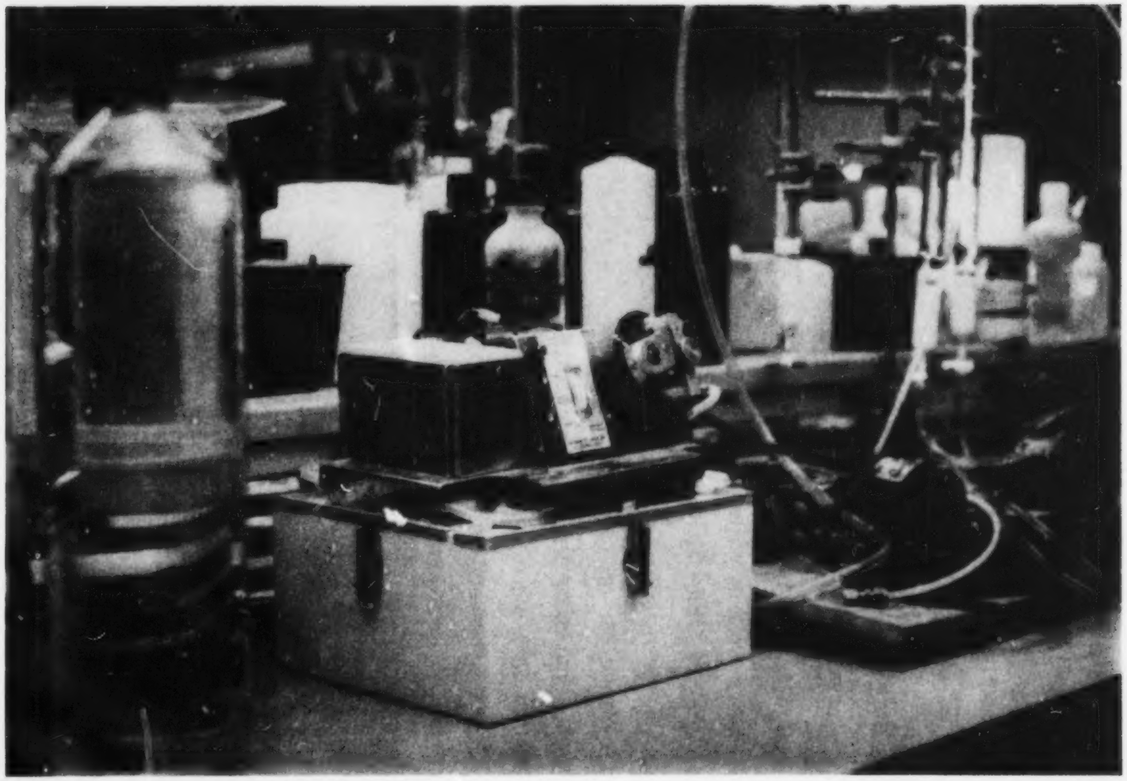


Figure 31. Automatic sampler.

up and overflow. The sampler lines were put in the beakers, also. Every hour the sampler would take a 200 ml sample, then purge the line of remaining water by reverse pumping back into the beaker. Since the beakers were just larger than the volume of samples taken, and the detention time in the beaker was approximately 4 minutes samples were fairly discrete.

$$4 \text{ minutes} = \frac{(250 \text{ ml})}{(62 \text{ ml/min})}$$

The "Wastewatcher" sample containers were analyzed for their ability to collect selenium samples and not effect the actual concentration of selenium present. Previously, known standards of selenium were stored with HNO_3 preservation in glass bottles and in "Qubetainers." The glass was able to store samples of selenium with ppb concentrations up to two weeks without any noticeable change, while samples stored in Qubetainers were reproducible for one week. The conventional polyethylene sample bottles from the "Wastewatcher" showed no measurable change in selenium concentrations in the ppb range for up to 48 hours. After this time, a loss of selenium was noticed. During the course of the 9-inch column runs, any samples collected in the "Wastewatcher" containers were analyzed within 48 hours after taking them. From time to time during the testing, duplicate samples were taken in the "Qubetainers," glass bottles, and the "Wastewatcher" sample bottles. No difference was noticeable between the three containers as long as they were analyzed within 48 hours after taking the sample.

Run Nos. 1-3: Capacity Tests at pH 5, 7 and 9

Runs 1 and 2 were conducted at stock pH's of 5, 7, and 9. During the initial part of run 3, there was a considerable amount of calcium carbonate build-up in the pH 9 column. The pH 9 run was discontinued after two hours during this run. These tests were done to check the varied capacities for Se(IV) over a wide pH range.

Run 1 used virgin media that had been acid rinsed prior to use. Figure 32 shows that the pH 7 column had the greatest capacity for Se(IV) in run 1, but dropped considerably in run 2. The breakthrough capacities for a stock concentration of 50 ppb Se(IV) after run 2 are estimated to be: pH 5 - 1500 bed volumes, pH 7 -900 bed

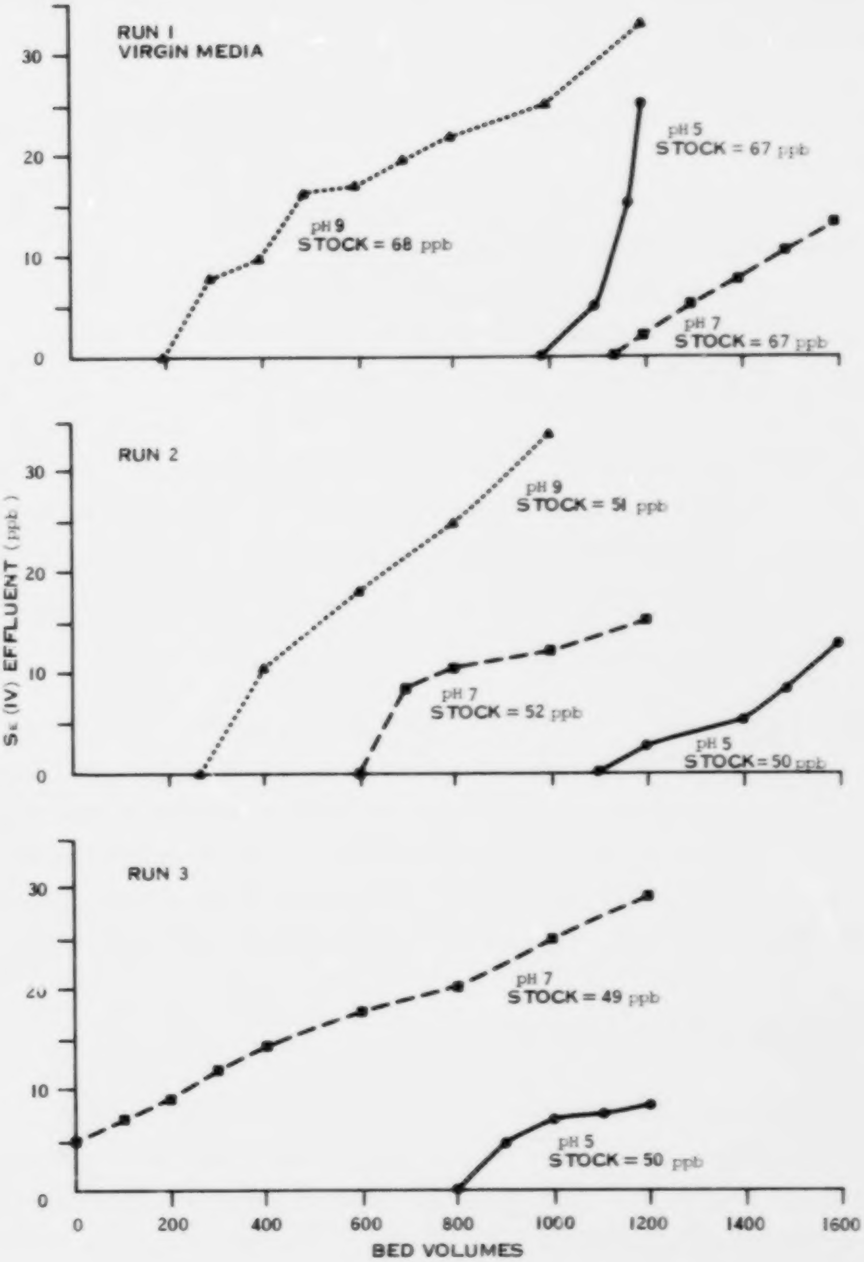


Figure 32. Run 1-3, Capacity Tests.

volumes, and pH 9 - 400 bed volumes. This equates to the following capacities for Se(IV) in terms of milligrams of Se(IV) per liter of activated alumina (mg/l): 67.5 mg/l, 40.5 mg/l, and 18 mg/l.

Based on the results from the 3-inch column studies, the regeneration after runs 1 and 2 was:

5 bed volumes of 0.5% NaOH at 3 gpm/ft^2, up
10 bed volumes of D.I. water at 3 gpm/ft^2, up
5 bed volumes of 0.05N H_2SO_4 at 3 gpm/ft^2, up
5 bed volumes of D.I. water at 3 gpm/ft^2, up

It is evident that the capacity for Se(IV) at pH 5 and 7 decreased in both cases and leakage of Se(IV) was 5 ppb for pH 7 during run 3. At pH 7, the breakthrough capacity dropped to 300 bed volumes (13.5 mg/l). Since the pH 5 run was terminated prior to 10 ppb breakthrough, its capacity can only be estimated as 1300 bed volumes (58.5 mg/l).

Table 13 includes a list of the removals and recoveries of Se(IV) during all the 9-inch column tests. This table will be referred to often in the remainder of this section. For runs 1 through 3, the amount of Se(IV) recovered during regeneration stays the same; approximately 1.9 mg for pH 5 and 2.9 mg for pH 7. Notice that the total amount of Se(IV) removed during each run steadily decreased. The recoveries ranged from 20 to 40 percent; obviously not as much was recovered as was removed.

Run No. 4: Capacity Test, pH 5, 6, and 7

Figure 33 shows run 4. Following run 3, the media used for the pH 9 runs was discarded and replaced with virgin media, which was rinsed with acid only. The breakthrough curve for pH 6 is longer than pH 5 or pH 7, approximately 1400 bed volumes (77 mg/l capacity for Se(IV) with C_i = 60 ppb). Capacity for pH 5 was 1100 bed volumes (60.5 mg/l) and 900 bed volumes for pH 7 (49.5 mg/l). The larger breakthrough capacity for pH 6 is attributed to the initial high capacity of the virgin media.

TABLE 13

SUMMARY OF REMOVALS AND RECOVERIES OF Se(IV) DURING ALL RUNS WITH 9-INCH COLUMNS

(Regeneration with 5 bed volumes of 0.5% NaOH at noted flow rate)

Run	Se(IV) Stock Con. (ppb)	Stock pH	Se(IV) Removed During Run (mg)	Se(IV) Recovered During Subsequent Regeneration (mg)	NaOH Flow Rate (gpm/ft^2)	% Recovery
1	68	5	9.3	1.8	3	19
	67	7	11.8	2.9		25
	67	9	6.9	2.4		34
2	50	5	8.7	2.1	3	24
	52	7	6.7	2.9		44
	51	9	4.4	3.5		79
3	50	5	6.3	1.8	3	29
	49	7	4.5	2.8		62
4	61	5	7.3	2.7	3	37
	62	6	7.5	2.3		31
	60	7	7.0	2.7		39
5	112	5	9.3	10.9*	1	117
	113	6	9.3	9.1		99
	115	7	9.1	8.9		97
6	110	5	12.3	8.8	1	72
	110	6	11.8	9.0		76
	111	7	11.9	5.9		50
7	210	5	17.7	7.7	1	43
	212	6	17.0	7.5		44
	205	7	16.7	8.0		48
8	211	5	22.6	6.8	1	30
	209	6	22.2	8.8		40
	206	7	21.8	8.7		40
9	190	5	21.3	8.1	1	38
	195	6	21.0	7.1		34

TABLE 13

(CONTINUED)

(Regeneration with 5 bed volumes of
0.5% NaOH at noted flow rate)

Run	Se(IV) Stock Con. (ppb)	Stock pH	Se(IV) Removed During Run (mg)	Se(IV) Recovered During Subsequent Regeneration (mg)	NaOH Flow Rate (gpm/ft^2)	% Recovery
10	215	5	26.3	7.9	1	30
	204	6	24.8	8.0		32
11	205	5	25.1	9.2	1	37
	201	6	24.0	10.2		43
12	195	5	23.1	9.0	1	37
	202	6	23.7	9.1		43
13	205	5	23.8	19.7	.5	83
	205	6	23.5	19.3		82
	200	7	14.9	13.1		88
14	201	5	29.5	20.5	.5	70
	198	6	28.6	19.9		70
	205	7	28.6	21.3		74
15	18200	5	1391.0	1154.0	.5	82
	18000	6	1195.0	1086.0		91
	18000	7	891.0	892.0		100
16	200	5	12.4	128.9	.5	--
	204	6	4.9	112.6		--
	210	7	-14.5	91.3		--
17	185	5	16.4	48.6	.5	--
	195	6	16.2	42.1		--
	192	7	13.3	36.9		--
18	200	5	19.1	35.2	.5	--
	204	6	19.2	31.4		--
	197	7	16.9	27.8		--

*Run #5 was completed as usual, but the columns were allowed to sit for 1 week prior to regeneration. The high figures would appear to be due to diffusion from the media into the surrounding water during this "rest period.

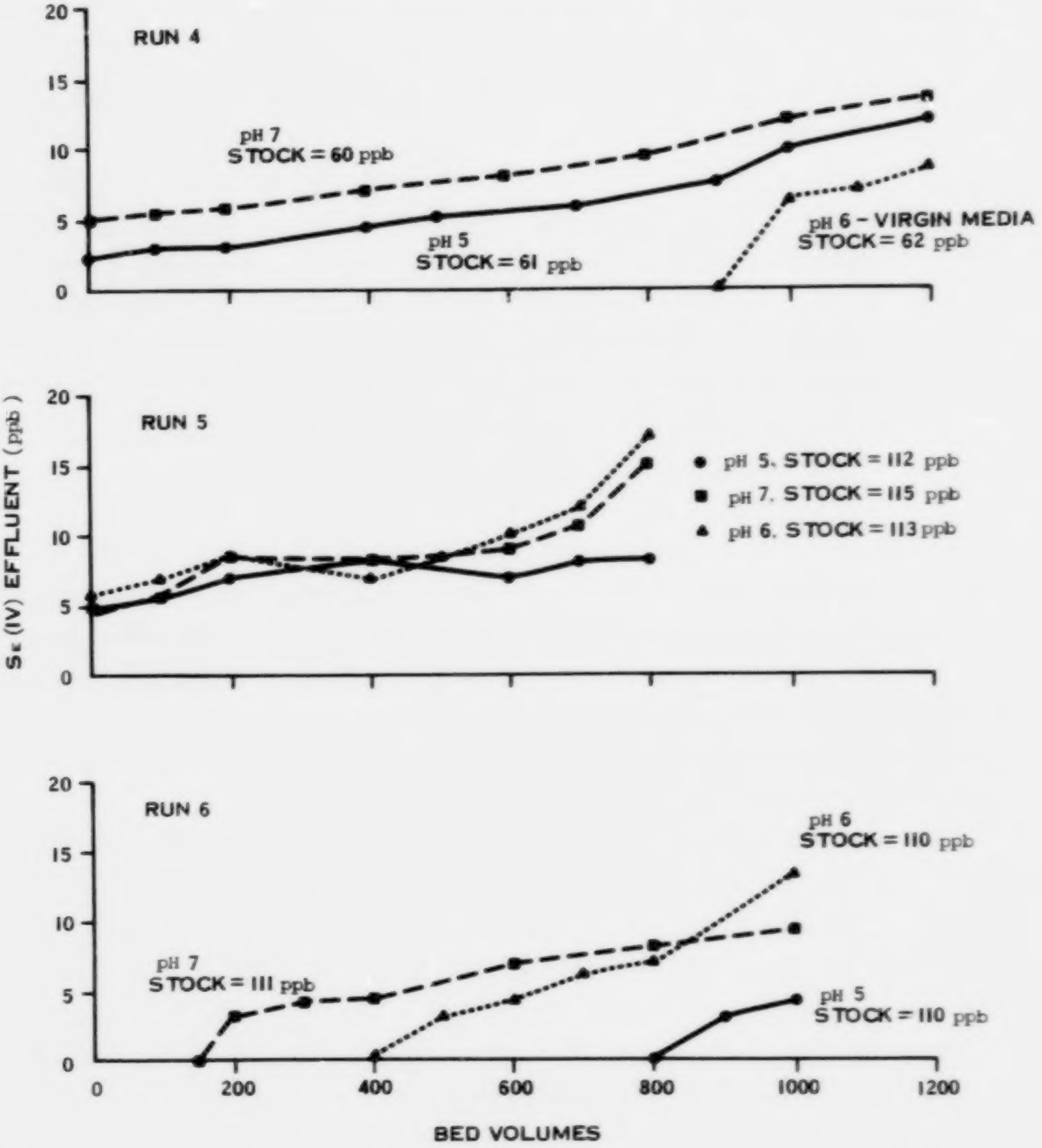


Figure 33. Runs 4 - 6, Capacity Tests.

Run Nos. 5 and 6: Capacity Tests, C_i = 100 ppb, 1 gpm/ft^2 NaOH

From runs 1 through 4, we observed two important points:

1) With the NaOH being applied at 3 gpm/ft^2, approximately 30% of the selenium was being recovered. If left in this cycle, the breakthrough curves would have continued to get worse, and the leakage would have increased until some equilibrium was established between the amount adsorbed during the run and the amount eluted during regeneration. To increase the amount of Se(IV) eluted, the flow rate was decreased to 1 gpm/ft^2. If diffusion plays a large role in the adsorption process, then lowering the flow rate threefold should recover at least three times the amount of Se(IV). For more discussion on the diffusion problem, reference is made to the section following runs 13-14.

2) In an effort to increase the slope of the breakthrough curve from shallow to steeper, the stock concentration was increased to about 100 ppb (= 0.10 mg/l). Expectedly, the amount of Se(IV) adsorbed should increase due to the increased "driving force." But by increasing the stock concentration, perhaps once the alumina had adsorbed as much as it could, a rapid breakthrough up to the influent concentration would be noticed.

Based on the above discussion, runs 5 and 6 were conducted with a stock concentration of Se(IV) of roughly 100 ppb and the subsequent regenerations with 1.5 #/ft^3 of NaOH at a flow rate of 1 gpm/ft^2. This lowered flow rate increased the flow-through time of the caustic in the bed from 10 minutes to 30 minutes.

Figure 33 shows runs 5 and 6. Because of the increased stock concentration and the fact that the previous regeneration was done at 3 gpm/ft^2, the resultant breakthrough pH 5 drifted slowly up, with no breakthrough to 10 ppb. After run 5, the columns were not regenerated immediately. The columns sat unregenerated for one week before elution. As seen in Table 13, the amounts recovered from the columns were at least equal to the amounts removed during run 5. The long rest period helped to diffuse some Se(IV) out of the alumina into the surrounding fluid.

The following run (Figure 33) shows that the leakage dropped to zero for all the pH's and that breakthrough bed volumes for pH 6 and 7 were 900-1000 (94.5-105 mg/l). Since the run was stopped prior to breakthrough with pH 5, breakthrough can only be estimated to occur at 1300 bed volumes (136.5 mg/l). Note that the amount removed during treatment increased significantly from run 5. The following regeneration recovered at least three times what the 3 gpm/ft^2 regeneration recovered in runs 1 through 4.

Run Nos. 7-12: Capacity Tests, C_i = 200 ppb, 1 gpm/ft^2 NaOH

Because the 100 ppb stock concentration didn't appear that it would rapidly produce a saturation of the alumina with Se(IV), and therefore not produce the desired rapid breakthrough, it was decided to jump to a 200 ppb stock solution. It was expected that the capacity of the alumina for Se(IV) would increase again, perhaps double from the removals seen with C_i = 100 ppb and four times as much as with C_i = 50 ppb. We were still trying to quickly fill up the sites on and in the alumina to achieve rapid breakthrough.

The initial run (#7) in this series with C_i = 200 ppb showed poor breakthrough characteristics, similar to what happened after we changed the stock from 50 ppb to 100 ppb in run 5. Figure 34 shows that during run 7, the pH 7 column exhibited no capacity to achieve an effluent concentration of less than 10 ppb. The breakthrough capacities for pH 5 and pH 6 were, respectively, 600 bed volumes (123 mg/l) and 500 bed volumes (102.5 mg/l).

Run 8 shows a greatly improved breakthrough curves, with leakage being 5 ppb, 2 ppb and 0 ppb for pH 7, 6, and 5, respectively. The breakthrough bed volumes increased to 500 (102.5 mg/l), 900 (184.5 mg/l), and 1100 (225.5 mg/l), respectively. The total amount of Se(IV) removed increased from run 7 to about 22 mg.

After run 8, one of the motors broke down and we decided to continue testing pH 5 and 6, as they seemed to produce the optimum removals. Subsequent runs 9 through 12 were run under the same condition. See also Figure 35. For these four runs, the average breakthrough capacity for pH 5 was 900 bed volumes (175.5 mg/l), and for pH 6 was 500 (97.5 mg/l).

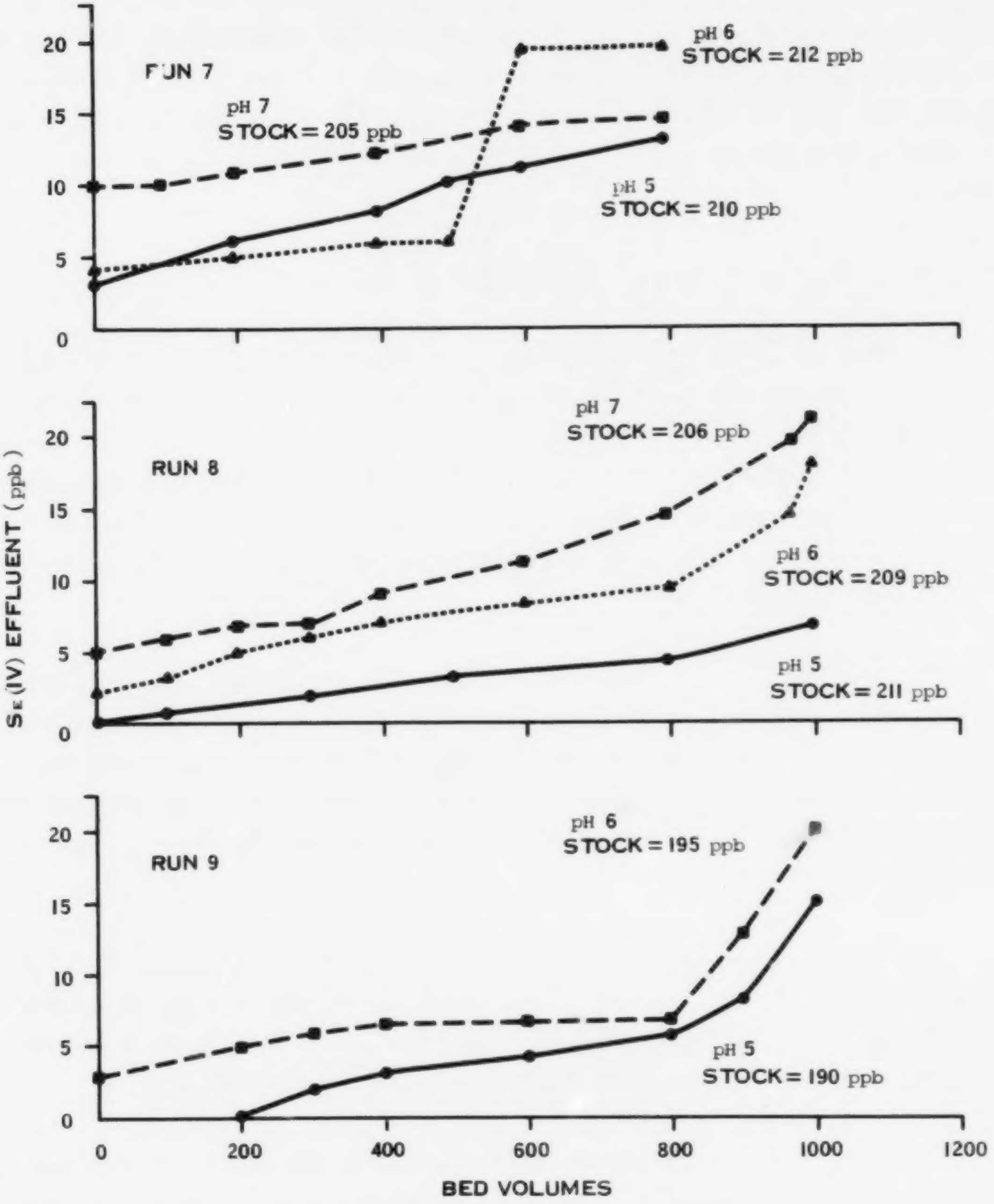


Figure 34. Runs 7 - 9, Capacity Tests.

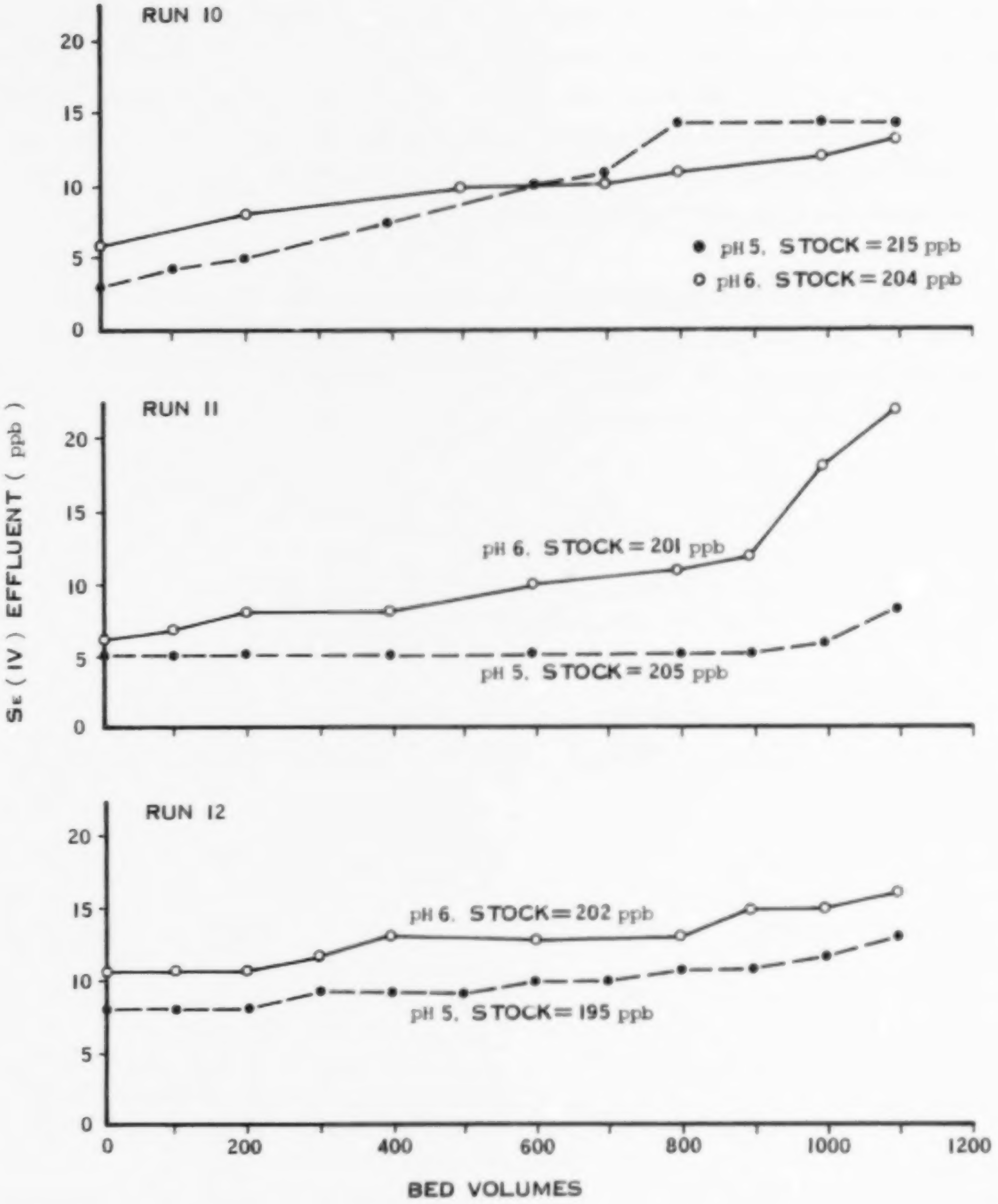


Figure 35. Runs 10 - 12, Capacity Tests.

Notice that for runs 9-12, there is a general trend of increased leakage and lower breakthrough capacity. If you look at the recoveries during these runs, the percent recovered averages approximately 37%. The amount recovered has not increased from the 100 ppb stock tests by the same factor that the amount removed has. The decreasing breakthrough capacities attest to the fact that the poor recoveries are affecting how the alumina performs in the following run. The slower regeneration rate (1 gpm/ft^2) was not slow enough.

During run 12, composite samples were taken of the first 500 bed volumes of the effluent for the three columns. These composites were analyzed for bicarbonate alkalinity, chloride, sulfate, nitrate, fluoride, and hardness. These were compared with the stock concentrations of each column. Results are listed in Table 14.

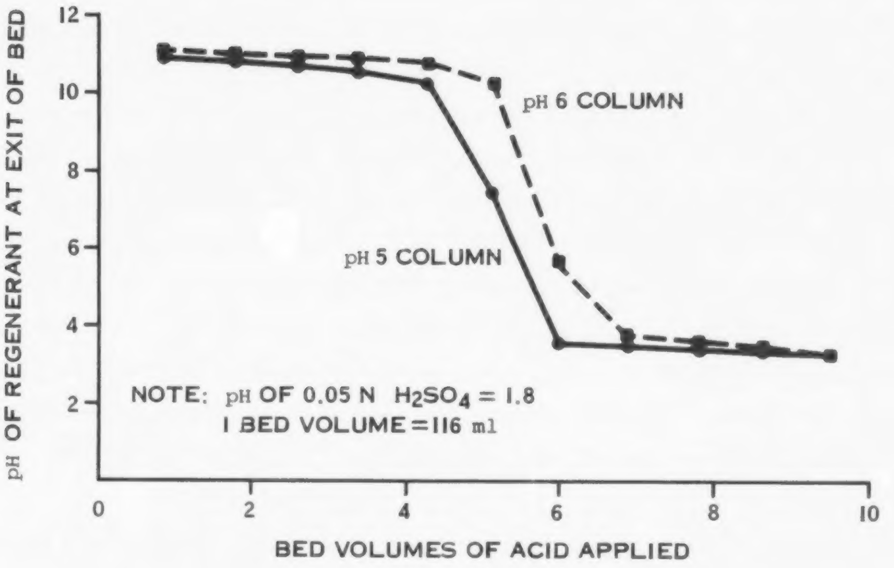
TABLE 14

COMPARISON OF REMOVALS OF INTERFERING ANIONS AND CATIONS DURING RUN 12

	pH 5		pH 6		pH 7	
Species	Influent	Effluent	Influent	Effluent	Influent	Effluent
Alkalinity (mg/l) (as $CaCO_3$	22.8	26.0	90.6	92.0	200.0	190.4
Chloride (mg/l)	402	420	359	361	312	311
Sulfate (mg/l)	98	97.3	96.6	109.3	102.6	102.6
Nitrate (as N) (mg/l)	4.5	3.3	4.8	2.9	4.5	3.2
Fluoride (mg/l)	0.85	0.15	0.90	0.20	0.89	0.40
Calcium (mg/l)	88.5	82.4	91.4	88.2	86.2	80.1
Magnesium (mg/l)	46.3	42.3	42.5	40.5	43.6	11.9

As seen, the levels of chloride remain fairly constant, except there is a slight rise at pH 5. Alkalinity and sulfate vary, with some levels increasing through the bed, others decreasing and some staying the same. This variation is not thought to be significant. However, decreases in nitrate and fluoride are seen in each run. Because of its low rank in the selectivity series, nitrate wasn't expected to be removed. However, because each column shows some removal and nitrate's detection limit very low (0.01 mg/l), the results show that activated alumina is removing some NO_3^-. The removal of fluoride is expected and greater removals were achieved at lower pH. The hardness ions, calcium and magnesium, decrease in each of the columns. This decrease, noted by other authors using activated alumina to remove fluoride, is thought to be due to secondary adsorption. The extremely low magnesium concentration at pH 7 is unexpected and may be due to poor analytical technique.

During runs 9-12, the acid rinse was analyzed more closely. Its objective is to reduce the pH of the bed to an operating level that will not reduce the capacity of the media for Se(IV). Rubel discovered that removal of fluoride begins to occur at pH's less than 10. His neutralization mode involved adjusting the pH of the raw water to be treated in steps to bring the pH of the treated water down to the pH of the raw water. In our system, we had no easy way to continuously adjust the pH of the stock feed solution. We tried to neutralize the bed with 0.05N H_2SO_4 until the pH of the bed dropped to around 7. In determining when this occurs, some very interesting facts came to light. Figure 36 shows plots of averages of the acid rinse waters' pH just out of the top of the bed versus the bed volumes of acid applied at 1 gpm/ft^2 (= 20 ml/min) for these four runs. Actually, pH was measured out of the teflon tube that fed the 2000 ml graduated cylinders to collect the regenerant. The pH out of the top of the bed was then back-calculated by subtracting the volume of the column and tubing above the top of the media. As can be seen, the pH decreased considerably near 5 bed volumes. While slowly decreasing for the first few bed volumes, the pH suddenly drops 6 or 7 pH units in 1 bed volume or less. At this point, the acid had neutralized most of the hydroxide ions from the caustic rinse. The pH seemed to level off at 3.5, and since the pH of the acid was 1.8, some neutralization of the acid must still have been taking place. To ensure that the pH of the bed dropped to at least 7, all ensuring runs were conducted with 6 bed volumes (700 ml) of 0.05N (0.25%) H_2SO_4 at 1 gpm/ft^2. This was also done in the upflow mode. It would not be necessary to do



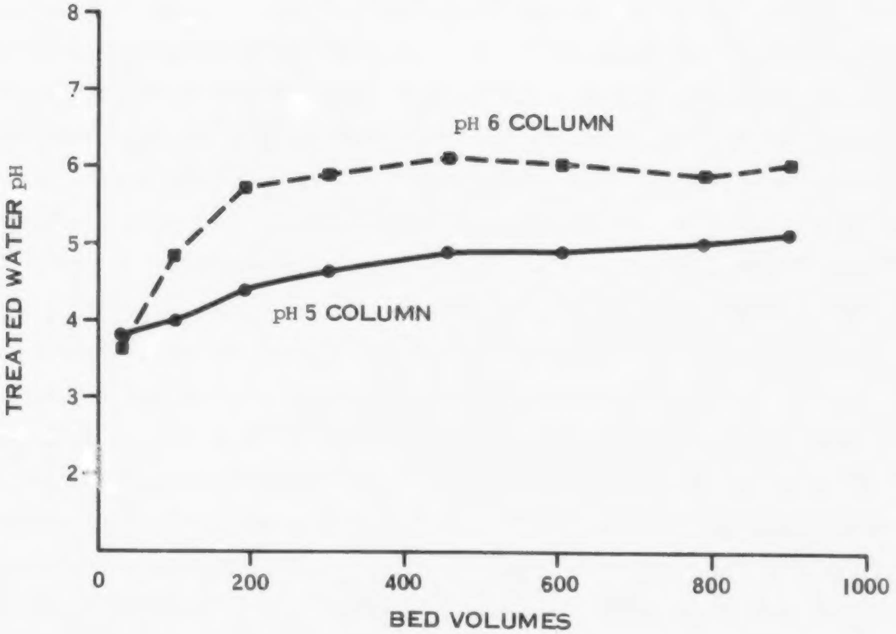


Figure 36. Neutralization of activated alumina by 0.05N H_2SO_4 and effluent pH of subsequent treatment run.

this in a large-scale removal facility. As a matter of fact, co-current acid rinsing would probably make the neutralization step more efficient by decreasing the chances for channelization. Up flow acid rinsing in these tests was done to keep the regeneration steps as simple as possible, without a lot of changes in tubing and pump arrangements.

Figure 36 also shows a plot of average effluent pH versus treated water bed volumes during the four runs, 9-12. The pH started to approach that of the stock solution immediately and levelled off at 300 bed volumes for pH 6 and 400 bed volumes for pH 5.

For a more economical use of the acid, this approach is suggested. Run 0.05N H_2SO_4 through the bed until the pH of the water at the exit of the bed is 10. Then start the treatment run with the pH adjusted raw water and let it bring the treated water pH down the rest of the way. The amount of time to bring the pH down will be short compared to the removal runs' length. A short operating time at a pH higher than the optimum, but below 10 will probably not affect the capacity of the alumina for Se(IV) to any great degree.

Run Nos. 13 and 14: Capacity Tests, C_i = 200 ppb, 0.5 gpm/ft^2

Run 13, shown in Figure 37 was conducted the same as runs 9-12, except that the broken motor had been replaced and testing of three pH's was resumed. However, the regeneration after run 13 was done at a 0.5% NaOH flow rate 0.5 gpm/ft^2. As explained previously, a slower regeneration was expected to significantly increase the amount of Se(IV) recoverable during regeneration. This regeneration took 60 minutes to accomplish, compared to 30 minutes for 1 gpm/ft^2 and 10 minutes for 3 gpm/ft^2.

Unexplainedly, the breakthrough curves for run 13 improved from run 12. 5 ppb, 2 ppb, and 0 ppb leakage were present in the pH 7, 6 and 5 columns respectively. The breakthrough volumes concurrently increased to 600 bed volumes (120 mg/l), 800 bed volumes (160 mg/l), and 1100 bed volumes (220 mg/l).

The amount of Se(IV) recovered in the regeneration after run 13 was more than twice as much as what was recovered during any of the 1 gpm/ft^2 regenerations.

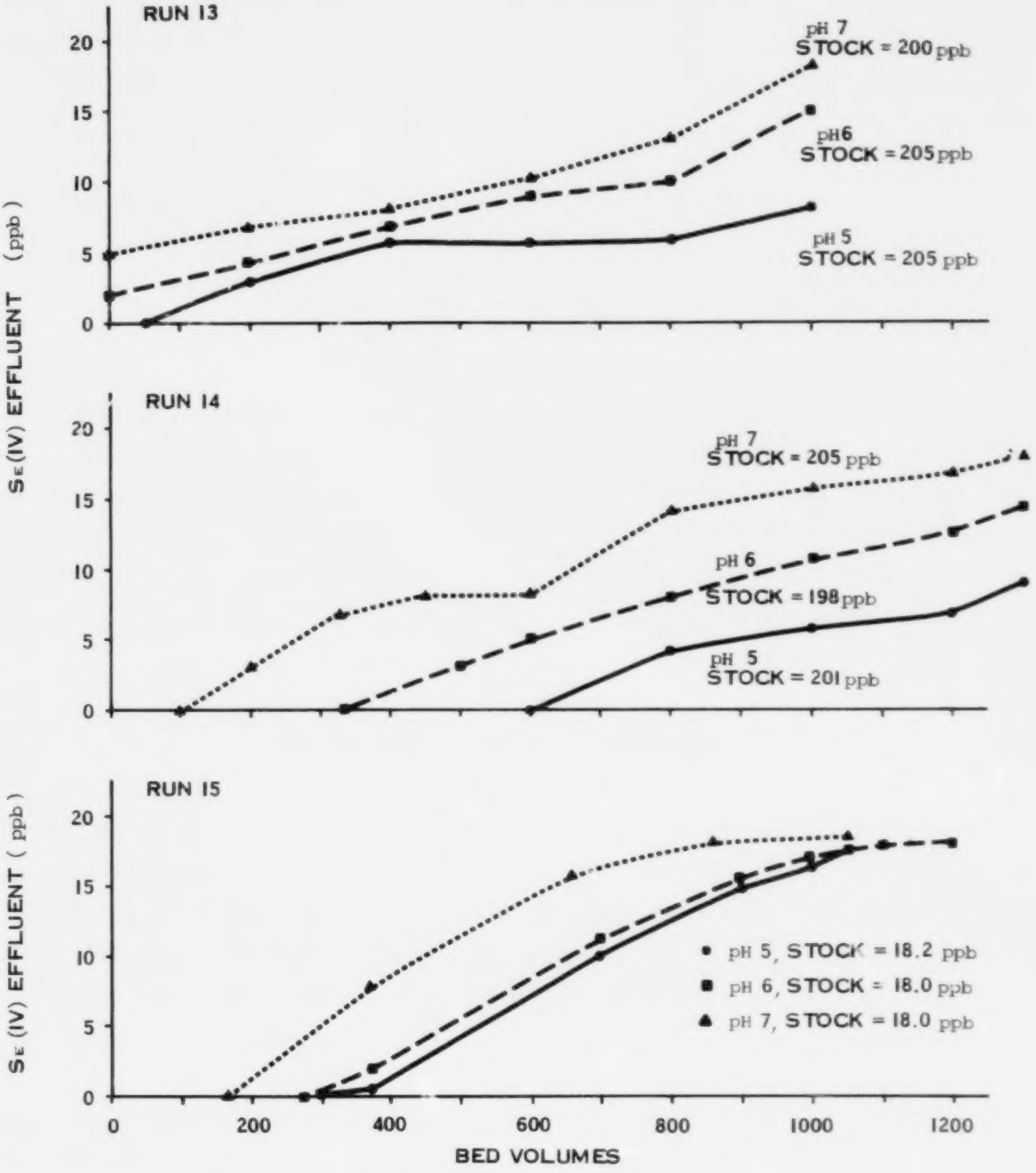


Figure 37. Runs 13 - 15, Capacity Tests and Saturation Test.

Obviously, the slower rate had quite an effect. Subsequent run 14 showed a vastly improved breakthrough curve, with no leakage for any of the columns and breakthrough bed volumes of 700 (136.5 mg/l), 1000 (195 mg/l), and 1400 (273 mg/l) for pH 7, 6, and 5, respectively. The regeneration after run 14 collected more Se(IV) than after run 13, but the percent recovery decreased due to the increased amount of Se(IV) removed in run 14 as compared to that of run 13.

The regenerant after run 13 was collected differently than after the previous runs. 100 ml aliquots of the regenerant after the NaOH rinse were collected to develop an elution curve. This curve, plotted as a percent of Se(IV) recovered during NaOH regeneration versus bed volumes, will tell a lot about whether kinetics play a large role in adsorption. If the curve has a very sharp peak, with very little "tail," then diffusion may not play a key role in regeneration. However, a curve with a long "tail" usually indicates that the regeneration is not as rapid and is controlled by diffusion.

Figure 38 plots data for the regeneration after run 13 for the three columns. The curves are corrected for the actual bed volumes of NaOH rinse and the deionized water rinse afterwards. The initial 200 ml of the regenerant collected was that water which was left over in the column when the treatment run was stopped. It had very little Se(IV) present. That volume was discarded and, as explained before, 100 ml aliquots were collected up to 1100 ml (9.5 bed volumes).

Note that the highest peak occurs earlier with increasing pH. This is probably due to the lower pH columns requiring more NaOH to initially bring the pH up to a level where OH^- ions are readily adsorbed by the media. As can be seen, the curves have long, drawn-out tails, suggesting that Se(IV) adsorption is diffusion-limited.

Based on these results so far, a discussion of the diffusion phenomena is presented in order to more clearly define the resistances to efficient mass-transfer in the adsorption process.

As explained by Weber[20], there are essentially three consecutive steps in the adsorption of materials from solution by porous adsorbents. Listed in order of occurrence, they are:

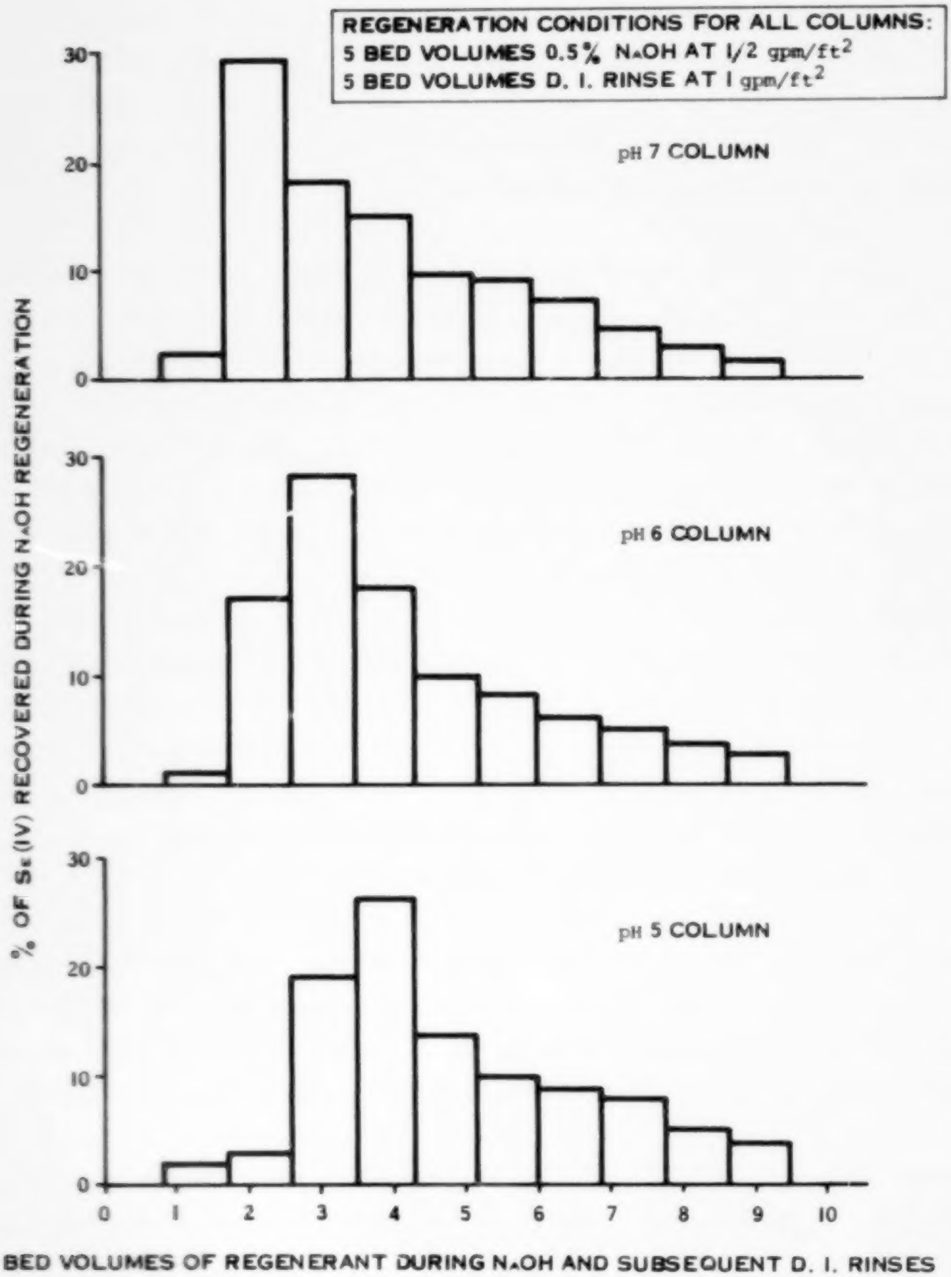


Figure 38. Elution curves for Regeneration after run 13.

1) Transport of the adsorbate through a surface film to the exterior of the adsorbent ("film diffusion")

2) Diffusion of the adsorbate within the pores of the adsorbent ("pore diffusion")

3) Adsorption of the solute on the interior surfaces bounding the pore and capillary spaces of the adsorbent.

After step 1, there will be a small amount of adsorption that occurs on the exterior surface of the adsorbent after transport across the surface film.

Investigations have suggested that the adsorption process itself (in activated alumina's case, the exchange of anions discussed in Chapter 1) is probably not rate-determining, and that a much slower process must control the overall rate of uptake.

Film diffusion describes the resistance to mass transfer in the region separating a turbulent bulk solution and a solid surface. Many theories have been postulated to explain this phenomena, but boundary layer theory seems to be the most plausible.

Since boundary layer theory accounts for a velocity distribution and is more realistic than theories which assume a laminar film surrounding the particle, it seems to be the best answer within today's knowledge.

Based on experimental evidence outlined by Weber, the rate of uptake of a solute by many porous adsorbents is governed by "intraparticle transport", the rate of transfer of adsorbed materials from the exterior sites of an adsorbent to surfaces bounding inner pore spaces. This was outlined in 2 as pore diffusion. The rate for diffusion processes can be expressed by Fick's first law,

$$F^o = - D_l \frac{\partial C}{\partial X} ,$$

where D_l is the diffusion coefficient

F^o is the mass transport through a unit cross-section in unit time (flux),

C is the mass concentration of diffusing substance, and

x is the space coordinate in the direction of diffusion, so

$\frac{\partial C}{\partial X}$ becomes the concentration gradient.

When this diffusion is accompanied by a surface process such as adsorption, then Fick's law must be modified to include a term for adsorption.

In relating the above discussion to our results, the effective removal of Se(IV) by activated alumina and its subsequent elution by NaOH seem to be controlled by the pore diffusion process. Figure 24 shows "plateaus" in the breakthrough curves and also increased removal for a short time after the columns had "rested." This would imply that significant film diffusion is occurring, with its co-current small amount of adsorption on the exterior surfaces. But when the concentration gradient between the surface and the interior of the alumina becomes sufficient, rapid particle diffusion depletes the surface layer, promoting a period of time during the run when the rate of increase in effluent concentration versus time decreases, i.e., the curve flattens out. If this column is allowed to rest overnight, the pore diffusion occurs deeper into the particles of alumina until a "semi-equilibrium" state is reached between the selenium molecules and the activated alumina. Restarting the column in the morning will repeat the above described process, but initially the alumina will be able to remove more Se(IV) due to the availability of sites within the pores closer to the surface of the alumina.

During elution of the Se(IV) saturated column with NaOH, a great difference in recovery was noted in the three different flow rates through the bed. By slowing down the NaOH flow within the bed while keeping the dosage of NaOH the same, the OH^- ions have more time to diffuse into the pores and exchange with the Se(IV) molecules.

In comparing the 1 gpm/ft^2 and 1/2 gpm/ft^2 rates, more than twice the Se(IV) was recovered in the slower regeneration. This implies that an even slower rate may recover even more Se(IV) than 1/2 gpm/ft^2. An optimum has not yet been found.

Based on the results of the batch kinetic tests, a smaller mesh (48-100) of activated alumina should appreciably improve the diffusion kinetics of a continuous flow column. The smaller particles have a larger total surface area per unit weight, therefore increased adsorption at the surface should occur. By adsorbing the Se(IV) more rapidly at the surface, the alumina should exhibit higher capacities. It would also make available more inner sites per unit weight. Unfortunately, 48-100 mesh is very fine and dissolution during regeneration would be greater. In addition to this, headloss during a treatment run would increase and the particles would be subject to washing out of the bed during backwash, if it is employed.

To effectively test the optimum dose and flow-through contact time of NaOH to regenerate Se(IV)-saturated alumina, one must continue decreasing the flow rate until no appreciable change in recovery is noted. Then, using this flow rate, vary the amount of NaOH applied (#/ft^3) until the maximum amount of Se(IV) is recovered. Both variables, of course, affect each other. It may be, that by using a slower flow rate (increasing the flow-through contact time of the NaOH), a much smaller amount of NaOH can eventually be used as the optimum regenerant dose. After diffusion was understood to be more significant than batch experiments indicated, time restrictions on this project forced us to delay this type of testing. We recommend that these tests be done in the future to completely investigate the diffusion phenomena and to further optimize NaOH flow rate and dose. An attempt was made to determine the operating characteristics of the columns in a "worst case" condition; as described in run 15.

Run 15: Saturation Test, C_i = 18 ppm

The remaining tests for Se(IV) were done to approximate the "worst case" condition, when the alumina has filled all its sites with Se(IV). The alumina was saturated with Se(IV) in run 15 with a stock concentration of approximately 18 mg/l. Figure 37 shows a fairly rapid breakthrough from 0 to 18 ppm for all the columns, with pH 7 breaking through faster than pH 6 and pH 5. Table 13 shows that almost

1,400 mg of Se(IV) were removed at pH 5, with 1,200 mg removed at pH 6, and 900 mg at pH 7. The following regeneration recovered 82, 91, and 100 percent of the Se(IV) removed in the pH 5, 6, and 7 columns, respectively. From the regeneration data, the 1/2 gpm/ft^2 NaOH regeneration would not elute all of the Se(IV) adsorbed during the previous saturation run. This would lead one to believe that the steady-state capacity for Se(IV) for the pH 5 and pH 6 columns was less than shown for run 14, with 1/2 gpm/ft^2 NaOH elution.

Run Nos. 16-18: Capacity Tests, C_i = 200 ppb, 1/2 gpm/ft^2 NaOH

After the saturation test, runs 16-18 show an approach to a steady-state condition where all of the Se(IV) would be recovered in regeneration that was adsorbed during the treatment run. The data in Table 13 show that the amount of Se(IV) removed during the treatment run increases as the alumina approaches an equilibrium between the Se(IV) removed and the Se(IV) recovered. Notice that for the 3 runs (Figure 39) following the saturation run, more Se(IV) is recovered in the regeneration than was removed in the previous treatment run. The differences in the two figures decreases as the cycles are continued, with run 18 suggesting that the amount removable and recoverable in a steady-state condition is probably 20 to 25 mg Se(IV). The breakthrough curves for the 3 different pH's are very different, with pH 5 producing more treated water with Se(IV) < 0.010 mg/l. The breakthrough for runs 16, 17, and 18 suggest that they will get progressively more bed volumes of treated water from each pH condition until steady-state is observed. Quite possibly, an even slower (< 1/2 gpm/ft^2) regeneration rate may be needed to remove enough Se(IV) to effectively prepare the alumina for a long enough removal run with sufficient breakthrough capacity.

Due to the time constraints on the project, it was necessary to initiate Se(VI) removal testing to get a good grip on the parameters of interest concerning Se(VI). Therefore, no further testing was done on Se(IV).

In conclusion, the ultimate capacity of activated alumina for Se(IV) will be a function of many variables: pH, dosage of NaOH, and NaOH regeneration flow rate. Depending on factors such as the cost of pH adjustment, the cost of chemicals, and the

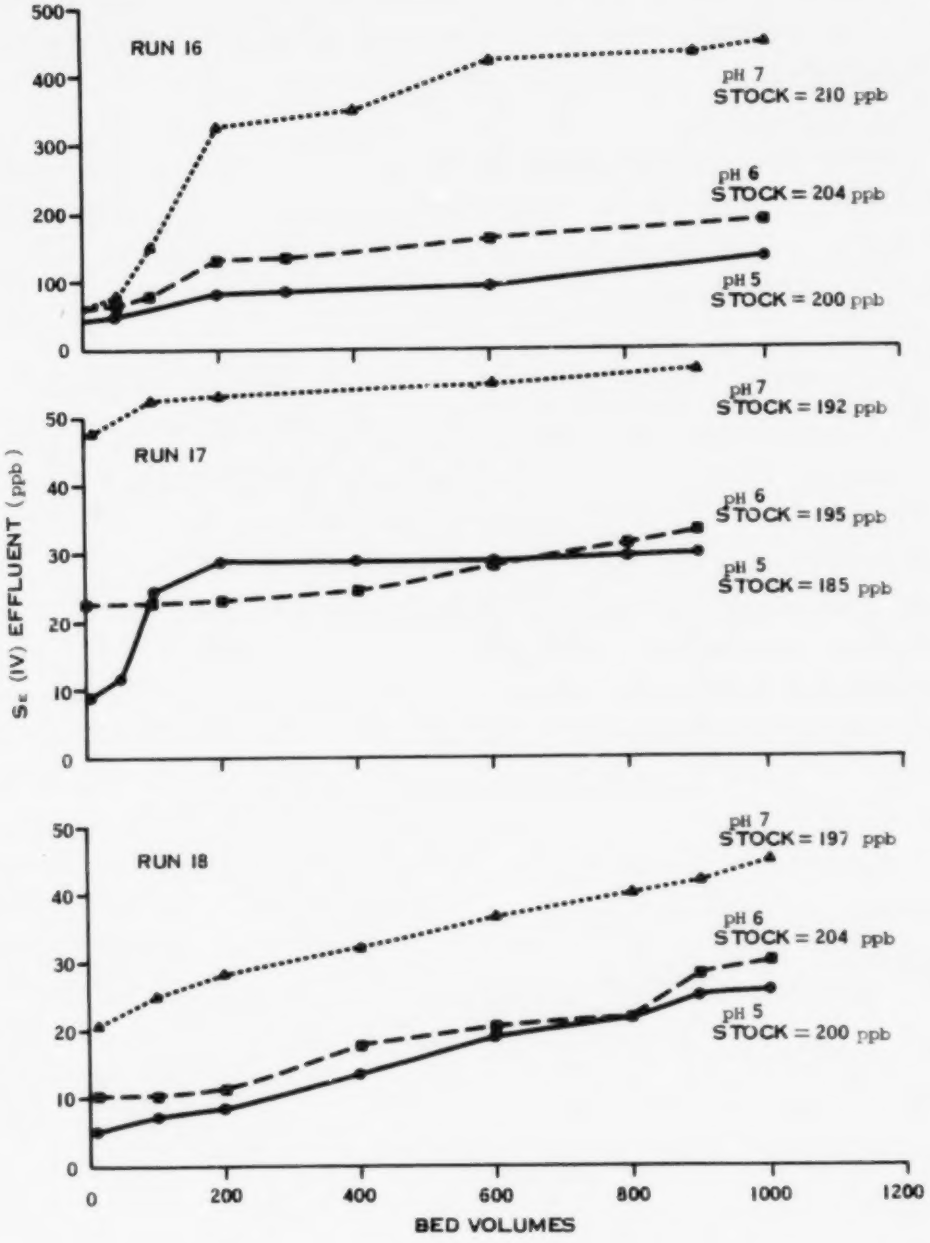


Figure 39. Runs 16 - 18, Capacity Tests.

influent Se(IV) concentration, an optimum operating plan may be different for two different sources of water. The kinetics of regeneration play the biggest role of any of the above-mentioned parameters in determining the ultimate capacity of activated alumina for Se(IV).

Based on data gathered during this phase of work, the following breakthrough capacities are estimated for an influent Se(IV) concentration of 200 ppb, with 0.5% NaOH regeneration at 1/2 gpm/ft^2 (a dose of 1.5 #NaOH/ft^3) and similar water quality to that tested in this study.

$$\text{pH 5 - 1,200 bed volumes} = 235 \frac{\text{mg Se(IV)}}{\text{liter of activated alumina}}$$

pH 6 - 900 bed volumes = 175 mg/l

pH 7 - 500 bed volumes = 100 mg/l

Work at lower concentrations suggested that similar breakthrough bed volumes for each pH could be achieved. This implies a linear relationship between adsorptive capacity and concentration. Some isotherm models predict a linear relationship between capacity and concentration, $q_e \propto c$, for very low amounts of adsorption. It is assumed that the levels of adsorption discussed in this report are low compared with adsorption of organics by activated carbon. We estimate that with lower concentrations of Se(IV) in the influent, capacities will be reduced. The following table predicts capacities for influent concentrations of Se(IV) of 50 and 100 ppb at the three pH's tested.

	50 ppb Se(IV)	100 ppb Se(IV)
pH 5	60 mg/l	120 mg/l
pH 6	45 mg/l	90 mg/l
pH 7	25 mg/l	50 mg/l

These capacities are all based on a 9-inch bed. Increasing the bed depth will probably increase the breakthrough capacity in bed volumes and should minimize leakage. Remember from Figure 24 that initial testing with 3", 6", 9" depths produced respectively, 600, 700, and 1100 bed volumes of treated water within Se(IV) concentration less than 0.01 mg/l at pH 6.5. This trend indicates that increasing the depth will increase the number of bed volumes produced prior to breakthrough. There will be some optimum level when increasing the depth provides no better removal. Pilot testing should verify this.

CHRONOLOGICAL SUMMARY OF Se(VI) REMOVAL TESTS USING 9-INCH COLUMNS

Run No. 1: Initial Test, 3-Inch Column

Prior to testing Se(IV) removal with 9-inch columns, and after testing Se(IV) removal with 3-inch columns, preliminary studies looked at rough estimates of Se(VI) removal. (Runs 1 through 5). Figure 40 (run 1) shows that the breakthrough was very rapid with a 3-inch column and the slope of the breakthrough curve was much steeper than with Se(IV). Since the run lasted only one-half an hour until breakthrough, it was immediately decided to try a deeper column of 9-inches.

Run Nos. 2 and 3: 9-Inch Columns, Repeatability Tests

Runs 2 and 3 (Figure 40) were done at pH 6.1 with a feed concentration of about 50 ppb Se(VI). The regeneration was as follows:

10 bed volumes D.I. water at 9 gpm/ft^2, upflow
27 bed volumes of 1% NaOH at 3 gpm/ft^2, upflow
10 bed volumes of D.I. water at 6 gpm/ft^2, upflow
16 bed volumes of 0.05N HCl at 3 gpm/ft^2, upflow
10 bed volumes of D.I. water at 6 gpm/ft^2, upflow

Remember that we had done no Se(IV) testing with 9-inch columns and had not optimized regeneration yet. However, HCl was used as the acid rinse because data from the batch tests showed HCl worked better for Se(VI) removal than H_2SO_4. Table 15 shows removals and recoveries for runs 2 and 3.

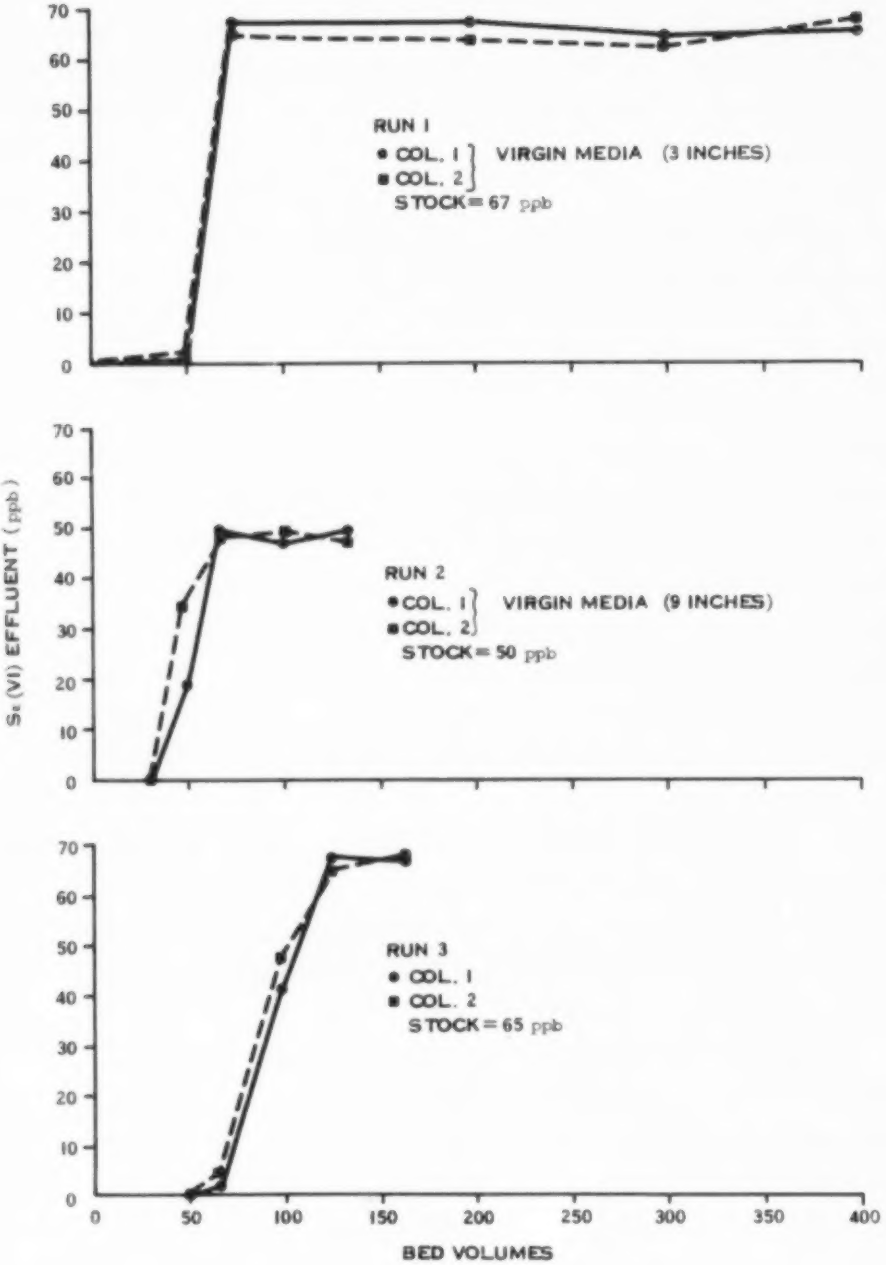


Figure 40. Runs 1 -3, Initial Tests.

It was apparent that the liberal amount of NaOH used to regenerate was sufficient to recover all of the Se(VI) removed during the previous run.

TABLE 15

REMOVALS AND RECOVERIES OF Se(VI) FOR RUNS 2 AND 3

Run	pH	Se(VI) Removed During Run (mg)	Se(VI Recovered During Subsequent Regeneration (mg)	% Recovery
2	6.1	0.28	0.35	100
	6.1	0.29	0.31	100
3	6.2	0.68	--	--
	6.2	0.65	--	--

Run Nos. 4 and 5: Regeneration Tests, Varied Amounts of NaOH

The regenerations after runs 3, 4, and 5 were done to delimit the amount of NaOH necessary to efficiently regenerate the column. 0.5, 5.3, and 53.0 bed volumes of 1 percent NaOH were tested to see if there were differences in recoveries. The flow rate was 3 gpm/ft^2 and the other regeneration steps were kept the same as before. Table 16 shows the removals and recoveries for runs 3, 4, and 5. Runs 4 and 5 are shown in Figure 41.

The data from these runs indicate that small amounts of NaOH (.5 bed volumes of 1 percent NaOH = $0.3 \frac{\#NaOH}{ft^3}$ can recover as much Se(VI) as the amount recovered using 100 times the applied dose of NaOH. Se(VI) is not as preferred by activated alumina as Se(IV) and, therefore, is much easier to recover during regeneration. Also, note that the treatment runs lasted on the order of one-tenth as long as the Se(IV) runs. This shortened run length limited the role that diffusion could play in adsorbing more selenium.

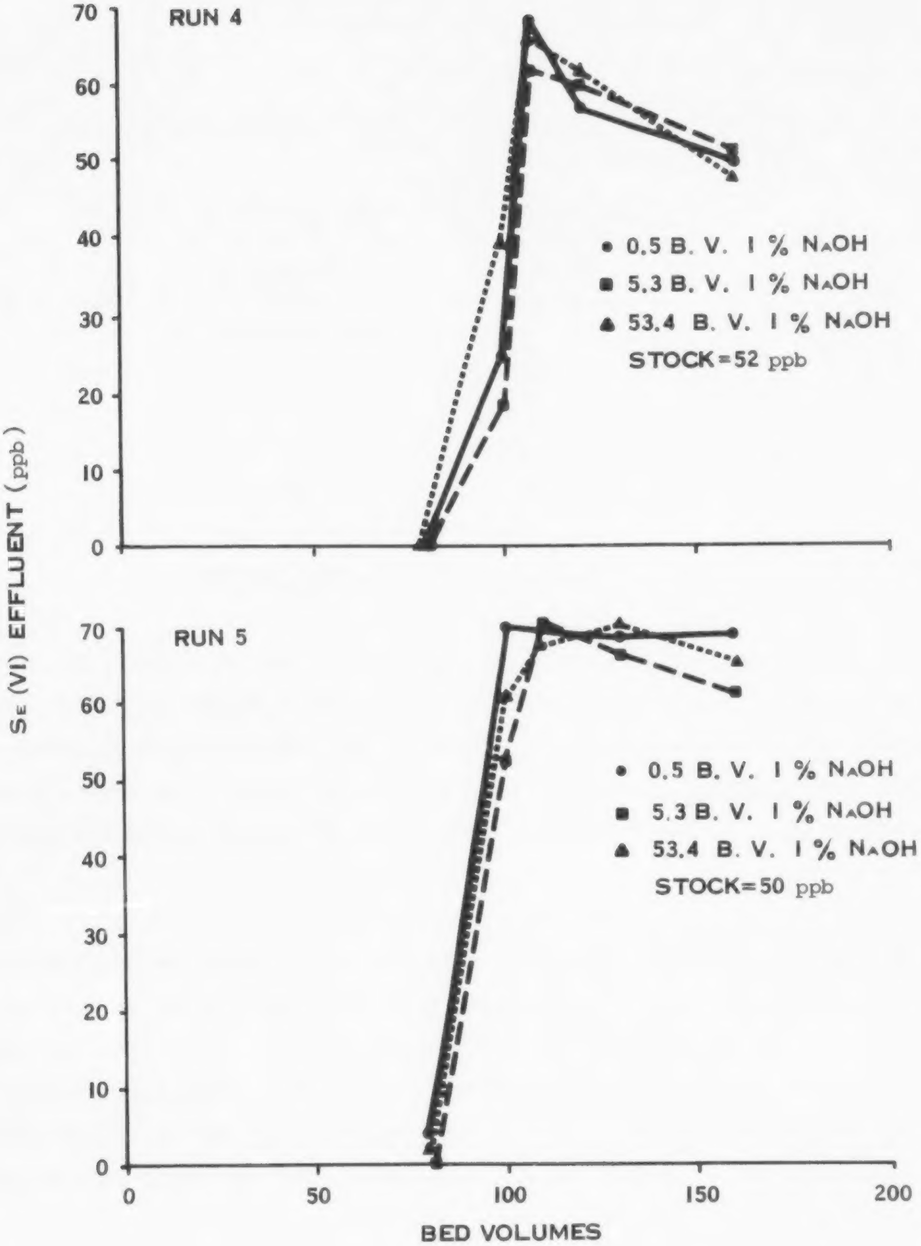


Figure 41. Runs 4 and 5, Regeneration Tests.

TABLE 16

REMOVALS AND RECOVERIES OF Se(IV) FOR RUNS 3, 4, AND 5

Run	pH	Se(VI) Removed During Run (mg)	Se(VI) Recovered During Subsequent Regeneration (mg)	Bed Volumes of 1% NaOH	% Recovery
	6.2	.68	.72	5.3	100
3	6.2	.65	.70	53.0	100
	6.2	.53	.50	0.5	94
4	6.2	.49	.52	5.3	100
	6.2	.51	.48	53.0	94
	6.2	.47	.50	0.5	100
5	6.2	.47	.45	5.3	96
	6.2	.49	.46	53.0	94

Run Nos. 6-8: Regeneration Tests, H_2SO_4 Versus HCl

Following run 5, Se(VI) testing was delayed until after the completion of Se(IV) testing. With the knowledge gained about Se(IV), we were able to quickly determine the important parameters concerning Se(VI) removal and regeneration. Based on Se(IV) data, the following regeneration scheme was adhered to throughout the remaining Se(VI) testing:

5 bed volumes of 0.5% NaOH, flow rate varied, up
5 bed volumes of D.I. water at 1 gpm/ft^2, up
6 bed volumes of 0.05N H_2SO_4 or HCl at 1 gpm/ft^2, up
5 bed volumes of D.I. water at 1 gpm/ft^2, up

Runs 6 through 8 (Figure 42) were regenerated prior to the treatment runs with H_2SO_4 as the acid rinse. As we noticed in the batch tests, a sulfuric acid rinse interferred with activated alumina's ability to adsorb Se(VI). Because SO_4^{-2} and SeO_4^{-2} are relatively close in the selectivity series for adsorption by activated alumina, the much greater concentrations of SO_4^{-2} (compared to SeO_4^{-2}) increased

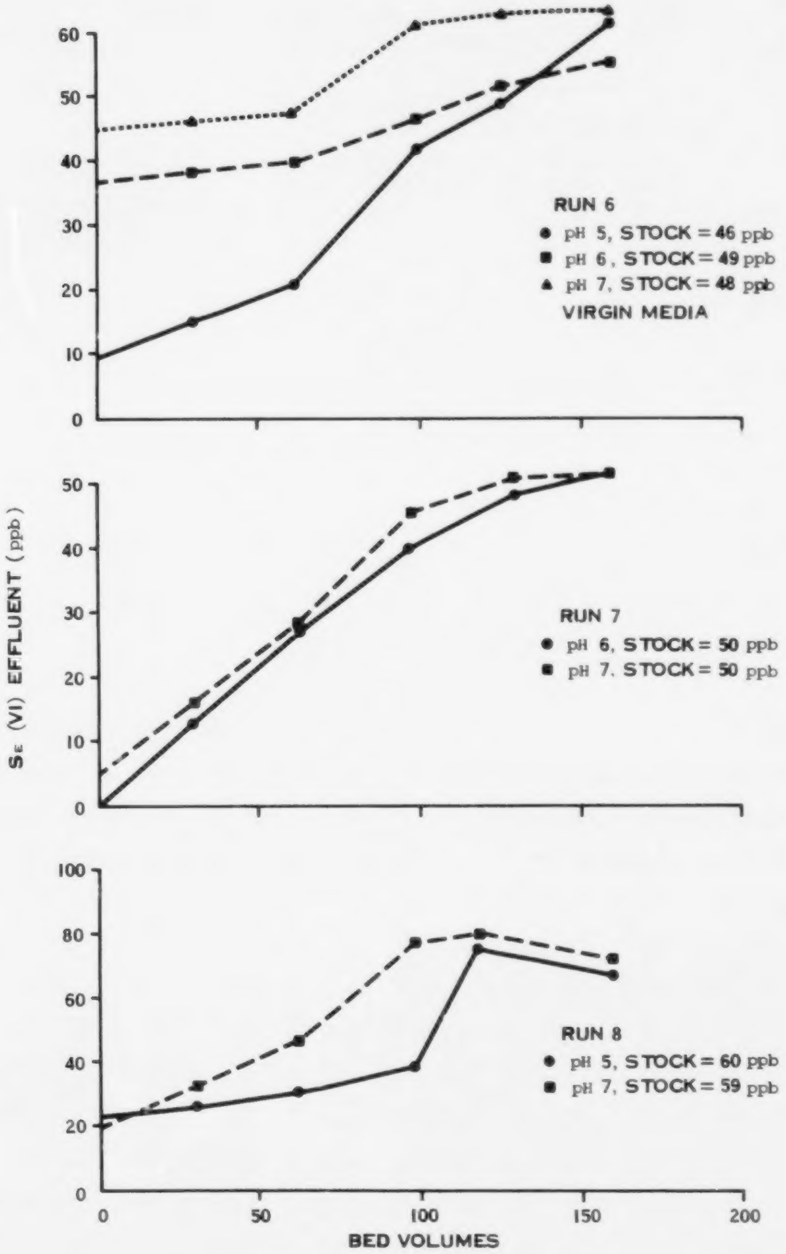


Figure 42. Runs 6 - 8, H_2SO_4 versus HCL regeneration.

its adsorption capacity in relation to SeO_4^{-2}. Therefore, the competition presented by SO_4^{-2} ions increases the difficulty of Se(VI) adsorption. The synthesized well water quality remained the same as in the Se(IV) removal runs.

The graphs indicate that pretreatment with H_2SO_4 will not produce any breakthrough capacity for Se(VI) at pH 5, 6, or 7. The alumina does adsorb some Se(VI), as shown in Table 17, but it didn't remove enough to bring the concentration lower than 10 ppb. Therefore, the regeneration following run 8 and all subsequent regenerations were done with a 0.05N HCl rinse. Chloride should not interfere with Se(VI) adsorption. During the regeneration after run 6, the motor for the pH 5 column broke down. No replacement was readily available and a new motor was not obtained until run 15 was initiated. pH 5 and pH 7 were done on runs 8 through 14, while the data for pH 6 was estimated by interpolation.

Run No. 9: Capacity Test, pH 5 and 7

The regeneration following runs 8 and 9 was done with the NaOH surface loading rate of 1 gpm/ft^2. It appeared as though the 1 gpm/ft^2 rate wasn't recovering all of the Se(VI). As with Se(IV), the amounts removed were calculated by integrating the area above the breakthrough curve and below the stock concentration level. Figure 43 shows run 9 and it is apparent that the concentration of Se(VI) increases above the stock concentration for a short period of time after breakthrough. This means that a more selective species is being adsorbed on the alumina causing the Se(VI) previously adsorbed to be desorbed, thus increasing the concentration of Se(VI) in the effluent. It is thought that $SO_4^=$ is causing this. In this case, after breakthrough has occurred, more Se(VI) is coming off than is being put on the column. This requires subtracting the amount desorbed after breakthrough from the amount adsorbed prior to breakthrough. The amounts of Se(VI) removed during the run shown in Table 17 reflect this calculation. From the graph, 100 bed volumes of treated water with an Se(VI) concentration less than 0.01 mg/l are produced at pH 5. This is equivalent to 4.5 milligrams of Se(VI) per liter of activated alumina. For pH 7, 35 bed volumes, or 1.6 mg/l Se(VI) were adsorbed.

Run Nos. 10 and 11: Regeneration Tests, 1/2 gpm/ft^2 NaOH

Because the regeneration at 1 gpm/ft^2 didn't appear to recover all of the Se(VI) removed during runs 6 through 9, the regenerations after runs 10 and 11 (Figure 43) were done at 1/2 gpm/ft^2. Table 17 shows that the amount of Se(VI) in the regenerant did not increase from the previous runs. Testing of Se(IV) regeneration showed that a decreased regeneration rate increased the amount recovered in the eluant. This was not found in runs 10 and 11.

Run Nos. 12 and 13: Regeneration Tests, 2 gpm/ft^2 NaOH

To verify that the kinetics of regeneration did not play as big a role as they did with Se(IV), regenerations after runs 12 and 13 (Figure 44) were done at 2 gpm/ft^2. As seen in Table 17, no change in the amount of Se(VI) recovered was noticed, but the apparent percentage of recovery still indicated that only 50 to 60 percent of the Se(VI) removed during a run was being recovered in the regeneration.

Run No. 14: Capacity Test, ph 5 and 7

We decided to collect all the effluent from both columns during run 14 (Figure 44). This represented 160 bed volumes or 18.6 liters of water for each column. The Se(VI) concentration in the composite samples for each column were: pH 5 - 45 ppb, pH 7 - 55 ppb. These amounts, subtracted from the initial concentration of Se(VI) in the stock solution and multiplied by the volume of effluent, should give the total amount of Se(VI) remaining on the alumina after termination of the run. The resultant amounts were: pH 5 - 0.26 mg, pH 7 - 0.09 mg. Table 17 shows that these amounts correspond to the amounts recovered in the regeneration after run 14.

The previous method for calculating the amounts of Se(VI) removed during the run was subject to some error, due to the small number of sample points on the breakthrough curve. Apparently, right after breakthrough, the curve goes much higher than the sample points indicate. There must be a very sharp peak immediately after breakthrough which made the integration by averaging the values of consecutive points inaccurate. Therefore, the amounts listed as Se(VI) removed during run for runs 6-13

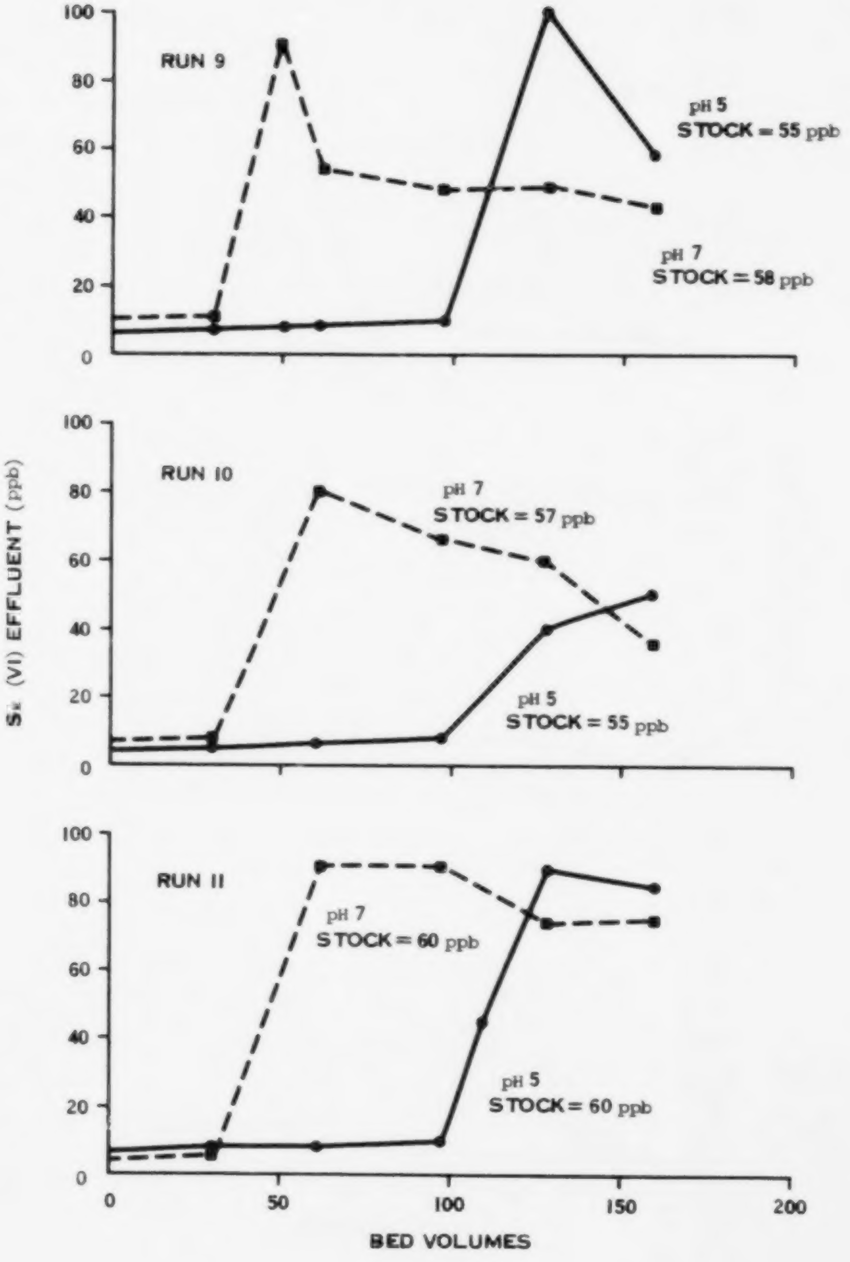


Figure 43. Runs 9 - 11, Regeneration Tests.

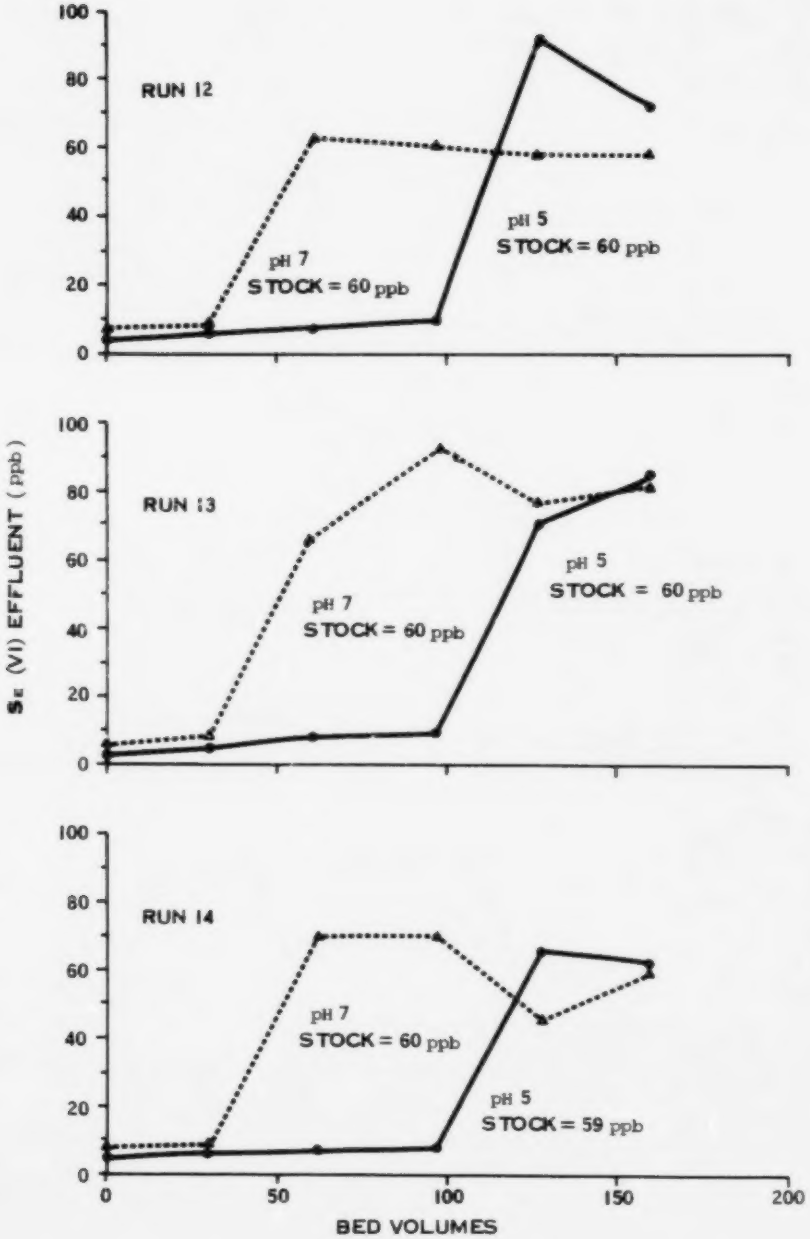


Figure 44. Runs 12 - 14, Regeneration Tests.

TABLE 17

REMOVALS AND RECOVERIES OF SE(VI) IN TESTS USING 9-INCH COLUMNS, RUNS 6-18

Run	pH	Se(VI) Removed During Run (mg)	Se(VI) Recovered During Subsequent Regeneration (mg)	NaOH Flow Rate (gpm/ft^2)	% Recovery
6*	5	0.22	0.17	1	77
	6	0.09	0.11		100
	7	0.01	0.02		100
7*	6	0.30	0.13	1	43
	7	0.21	0.09		43
8*	5	0.33	0.19	1	58
	7	0.17	0.20		100
9	5	0.40	0.25	1	63
	7	0.16	0.12		75
10	5	0.45	0.24	.5	53
	7	0.15	0.11		73
11	5	0.43	0.24	.5	56
	7	0.10	0.12		100
12	5	0.44	0.23	2	52
	7	0.15	0.12		80
13	5	0.45	0.23	2	51
	7	0.11	0.10		91
14	5	0.26	0.24	.5	92
	7	0.09	0.09		100
15	$6(SO_4^{-2} = 5)$	2.50	2.15	.5	85
	$6(SO_4^{-2} = 50)$	0.73	0.68		93
	$6(SO_4^{-2} = 500)$	0.06	0.04		67
16	$6(SO_4^{-2} = 5)$	2.45	2.13	.5	87
	$6(SO_4^{-2} = 50)$	0.69	0.63		91
	$6(SO_4^{-2} = 500)$	0.05	0.04		80

TABLE 17

(CONTINUED)

Run	pH	Se(VI) Removed During Run (mg)	Se(VI) Recovered During Subsequent Regeneration (mg)	NaOH Flow Rate (gpm/ft^2)	% Recovery
17	6(Alk = 5)	0.52	0.48	.5	92
	6(Alk = 50)	0.32	0.28		88
	6(Alk = 500)	0.18	0.15		83
18	6(Alk = 5)	0.57	0.53	.5	93
	6(Alk = 50)	0.27	0.27		89
	6(Alk = 500)	0.14	0.14		100

*Prior to these runs, 0.05N H_2SO_4 was used as the acid rinse. The removals of Se(VI) were resultantly low.

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are probably in error to some degree, and it is likely that 100 percent recovery by the regenerations may have been accomplished. The remaining four runs (15-18) had the effluent samples analyzed every hour as before, but all of the effluent was collected and analyzed, as per run 14.

Notice for runs 9 through 24 that leakage is present in all the runs. This leakage didn't affect the breakthrough volumes of any run since the effluent concentration of Se(VI) never got above 10 ppb until the rapid breakthrough. We assumed that all the Se(VI) was being removed during regeneration, so there should not be any present as leakage. Leakage was not present in runs 1 through 5 when the HCl acid rinse was initially used to treat the virgin media. It is possible that the H_2SO_4 rinses prior to runs 6 through 8 affected the performance of the following runs.

Based on the data acquired in runs 9 through 14, the following breakthrough capacities are estimated at pH 5, 6, and 7: 100 bed volumes, 65 bed volumes, and

30 bed volumes, given the water quality explained in Table 4 and an initial concentration of 50 ppb Se(VI). These volumes correspond to the following capacities: pH 5 - 4.5 mg/l, pH 6 - 3.0 mg/l, and pH 7 - 1.5 mg/l.

Similar to the data presented in Figure 38 for Se(IV), an elution curve was prepared for the regeneration after run 14. Because the kinetics of the regeneration did not play an important role in the recovery of Se(VI), it was assumed that the elution curve would show a sharp peak with very little tail. Compared with Se(IV), Se(VI) is not adsorbed nearly as well, therefore it makes sense that it should be easier to desorb.

Figure 45 shows that the elution curves for the pH 5 and 7 columns are almost identical in shape, with no relevant elution occurring after 2.5 bed volumes. The sharp peak occurred almost instantaneously with the first amount of NaOH that was applied. From this graph, it is apparent that OH^- ions are much preferred over Se(VI) ions and that the rate of application of the NaOH is not important. Probably much less NaOH could be used to effectively regenerate Se(VI), based on these results and earlier testing done with 0.5, 5.3, and 53.0 bed volumes of NaOH at 3 gpm/ft^2. To ascertain what minimum dose of NaOH would be appropriate to regenerate these columns, side-by-side tests with decreasing amounts of NaOH applied should be done. When less than 100% recovery is noted, it will indicate that the minimum dose has been used.

Because HCl would be the required acid for neutralization of the alumina in a full-scale removal facility removing a combination of Se(IV) and Se(VI), in order to optimize removals, its use had to be compared to that of H_2SO_4. A pH breakthrough diagram was constructed, similar to Figure 36 for 0.05N HCl during the regeneration, after run 14. Figure 46 shows the results. The amounts of HCl required to reduce the pH of the alumina after the 1/2 gpm/ft^2 NaOH regeneration are virtually identical to those for H_2SO_4. We expect no decrease in the capacity of activated alumina for Se(IV) due to the use of HCl. Cl^- is lower on the selectivity series than $SO_4^=$ and using this as the acid rinse may enhance Se(IV) adsorption.

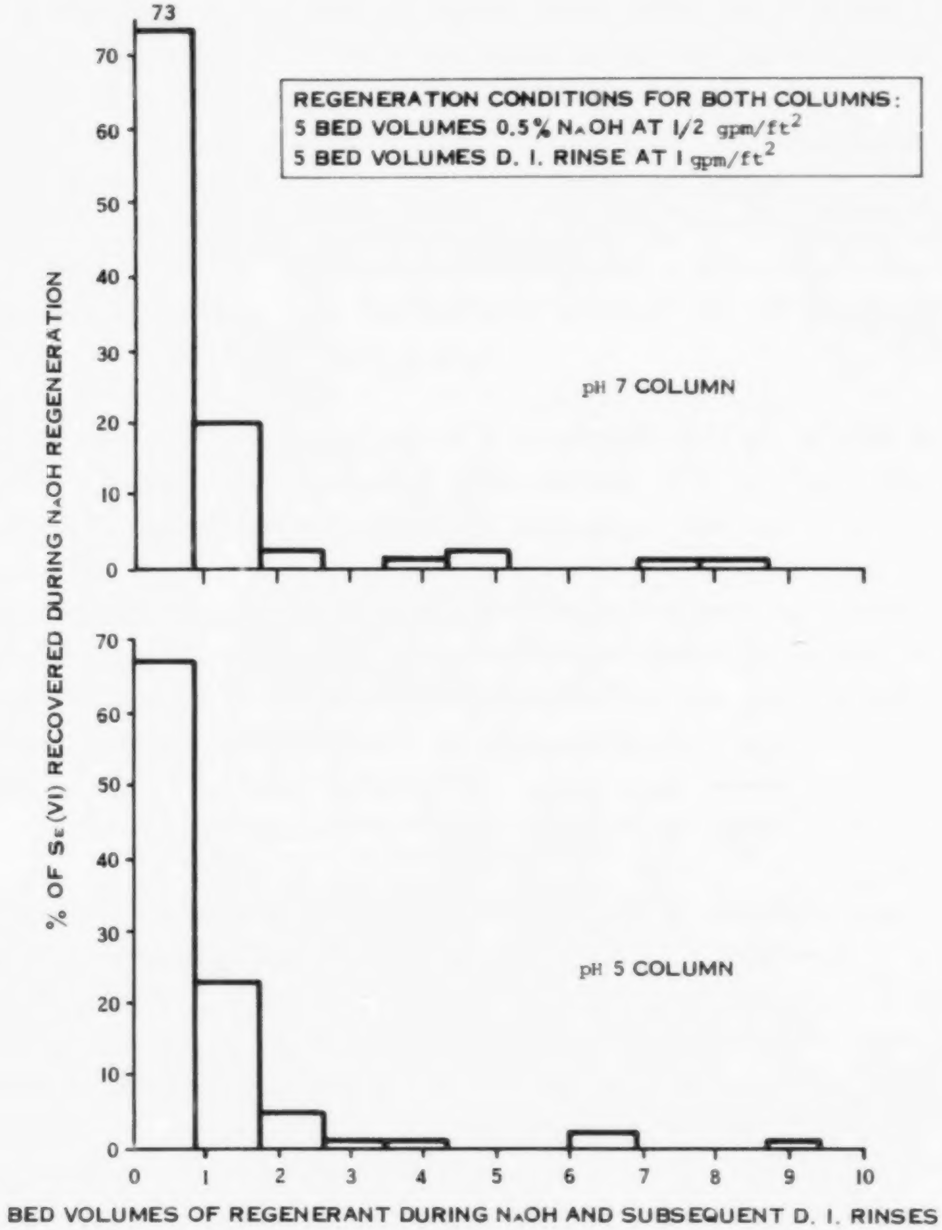

Figure 45. Elution curves for regeneration after run 14.

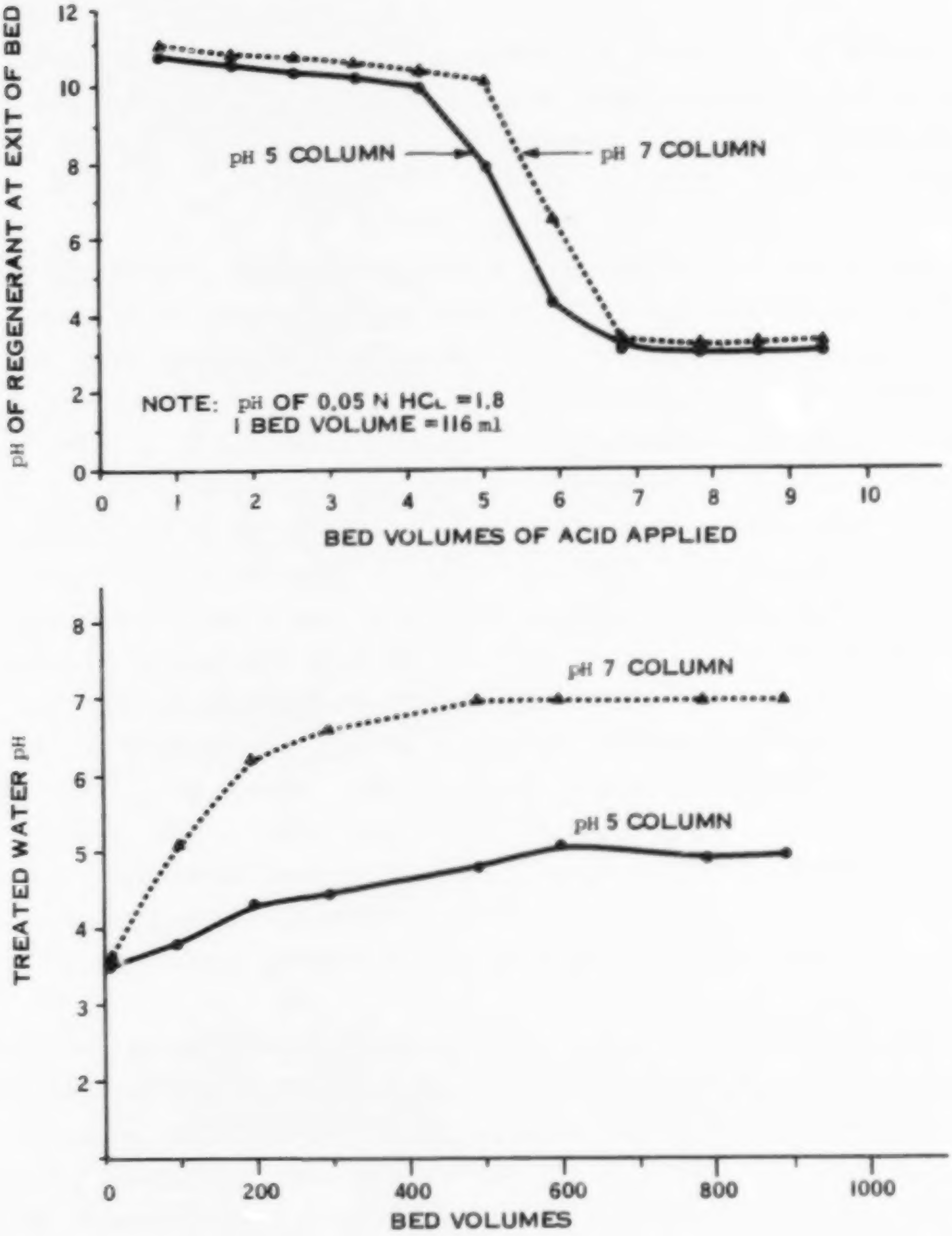

Figure 46. Neutralization of activated alumina by 0.05 HCL and subsequent treatment run.

Run Nos. 15 and 16: Sulfate Interferences

Because it was noted that sulfate and bicarbonate interfered with Se(VI) adsorption in batch tests and that rinsing with H_2SO_4 prior to a treatment run causes poor removal of Se(VI), it was decided to test varied levels of SO_4^{-2} and HCO_3^- for a few runs.

Runs 15 and 16 were done with sulfate concentrations of 5, 50, and 500 ppm SO_4^{-2} at a pH of 6 (see Figure 47). All other species in the synthesized water were kept the same as the previous tests. Remember that in the previous tests, the sulfate concentration was kept at approximately 100 ppm. Figure 42 shows that sulfate levels drastically affect the adsorption capacity of alumina with respect to Se(VI). At 500 ppm SO_4^{-2}, virtually no breakthrough capacity was available for Se(VI). At 50 ppm sulfate, 130 bed volumes of capacity is available until breakthrough. This was twice the capacity found for pH 6 with 100 ppm SO_4^{-2}. With 5 ppm sulfate, there is an entirely different type of breakthrough. No sharp increase in the amount of Se(VI) was present in the effluent, rather a very flat-sloped line that gradually increases in concentration is noticed. Breakthrough occurred at approximately 400 bed volumes. The level of competition between the SeO_4^{-2} and SO_4^{-2} has dropped to allow sites available for SeO_4^{-2}. The concentration ratio between SeO_4^{-2} and SO_4^{-2}, (SO_4^{-2}/SeO_4^{-2}), was roughly 100, whereas the ratios of 50 and 500 ppm So_4^{-2} were 1,000 and 10,000 respectively. Decreasing the sulfate level descreased its adsorption intensity enough to allow SeO_4^{-2} a chance to combine with activated alumina. This effect was the most dramatic of any of the tests performed in this study.

Figure 48 plots the relationship between either the ratio of sulfate or alkalinity to Se(VI) concentration and the capacity of the activated alumina to adsorb Se(VI). The alkalinity portion will be discussed later. At low ratios of sulfate to selenate, the capacity is greatly increased. For $SO_4^{=}$ to Se(VI) ratios of 1,000 or greater, it appears that there is a linear relationship between capacity and ratio. This was exhibited in the data for 50 and 100 ppm sulfate.

Note in Table 17 for runs 15 and 16 that due to the increased run length (15-16 hours) for the 5 ppm SO_4^{-2}, the 1/2 gpm/ft^2 NaOH regeneration didn't recover

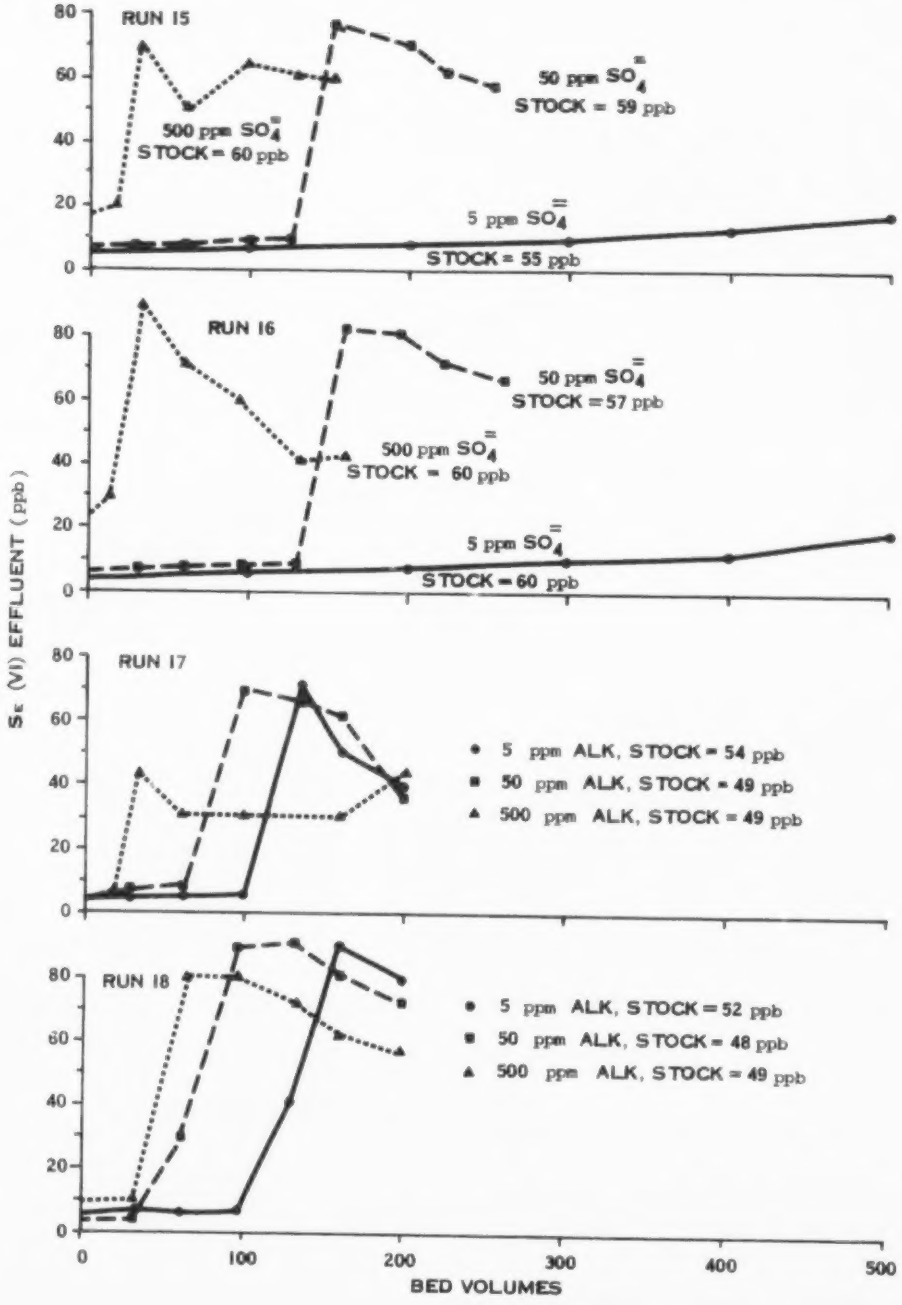

Figure 47. Runs 15 - 18, SO_4 and HCO_3 interferences.

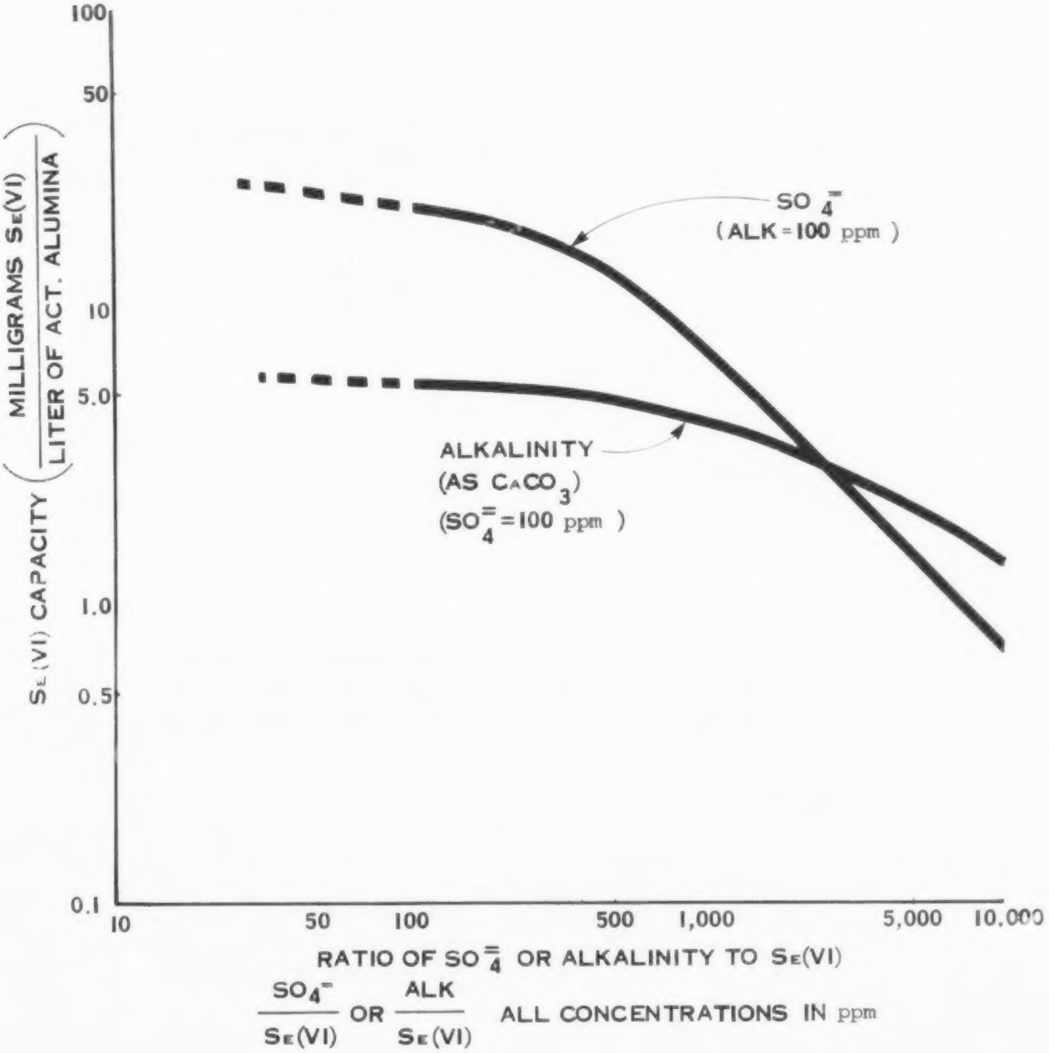

Figure 48. Se(IV) removal versus $SO_4^=$ and alkalinity concentrations.

all of the Se(VI) adsorbed. Diffusion allowed some of the Se(VI) to penetrate far enough into the bed to escape desorption by the NaOH. The shorter runs did not allow enough time for significant diffusion to occur, and all of the adsorbed Se(VI) was recovered.

Run Nos. 17 and 18: Alkalinity Interferences

The final series of tests were done to test alkalinity's effect on Se(VI) adsorption. The other parameters in the synthetic water were kept as before ($SO_4^{=}$ = 100 ppm) and only the alkalinity was varied to achieve 5, 50, and 500 ppm alkalinity (as $CaCO_3$) at pH 6. This required adding varied amounts of $NaHCO_3$ to each solution, as the amount of buffering capacity each system had would vary, and different amounts of HCl must be added to achieve the desired alkalinity at pH 6. For 100 liters of water, the following amounts of $NaHCO_3$ and HCl were added:

5 ppm - .33 meq/l HCO_3^- = 2.8 grams $NaHCO_3$

.23 meq/l H^+ = 3.9 ml of 6N HCl

50 ppm - 2.72 meq/l HCO_3^- = 22.9 grams of $NaHCO_3$

1.72 meq/l H^+ = 28.7 ml of 6N HCl

500 ppm - 33 meq/l HCO_3^- = 277.2 grams of $NaHCO_3$

23 meq/l H^+ = 383.3 ml of 6N HCl

The results are shown in runs 17 and 18 (Figure 47). The effect of varied HCO_3^- concentration is not as dramatic as seen with SO_4^{-2}. Apparently, the 100 ppm SO_4^{-2} in this water played the major role in determining the capacity. For 500 ppm alkalinity, 20 bed volumes of treated water with Se(VI) 0.010 mg/l was produced. For 50 ppm alkalinity, 65-70 bed volumes are produced and for 5 ppm alkalinity, 100 bed volumes are produced. The effect of reducing the alkalinity from 100 ppm to 50 ppm was barely noticeable, comparing results obtained in the previous runs. Figure 48 shows the relationship of alkalinity to Se(VI) capacity. Compared with the plot for sulfate, its effects are not as great.

In summary, Se(VI), being lower in the selectivity series, is more susceptible to interferences with adsorption. For the same operating conditions and water composition, Se(VI) was removed about one-tenth as much as Se(IV). Based on data gathered during Se(VI) testing, the following breakthrough capacities are estimated for an influent concentration of 50 ppb Se(VI), with 0.5% NaOH applied as the regenerant at 2 gpm/ft^2 (a dose of 1.5 #NaOH/ft^3), a neutralization step using HCl as the acid, and similar water quality to that tested in this study.

pH 5 - 100 bed volumes = $4.5 \ \frac{\text{mg Se(VI)}}{\text{liter of activated alumina}}$

pH 6 - 70 bed volumes = 3.2 mg/l

pH 7 - 35 bed volumes = 1.6 mg/l

These capacities are 13 times less than Se(IV) adsorption under similar conditions. If sulfate concentrations in the water are less than those used in this testing, (<100 ppm), increased capacity can be expected. If sulfates were present at 50 ppm, then the above capacities could be doubled. Alkalinity does not play as important a role in interferring with Se(VI) adsorption.

It is also predicted that for increased Se(VI) initial concentrations, the capacity for Se(VI) will linearly increase, as explained in the summary of the Se(IV) testing. However, the actual number of bed volumes of treated water with Se(VI) concentration less than 0.01 mg/l would remain the same.

Based on the results of these tests, Se(VI) would be the limiting factor in determining the capacity of activated alumina for a mixture of Se(IV) and Se(VI). If concentrations of Se(VI) exceeded 0.01 mg/l in the influent to a full-scale removal facility, then the run length would be limited to the breakthrough capacity of Se(VI).

Regeneration would therefore be required more often, with resultant increased costs due to chemicals and replacement of bed media.

One last test was performed on the activated alumina after the runs had been completed for approximately 1 week. The remaining media in the columns was mixed together, then 9-inches was put into the three columns. Another test was done with different concentrations of NaOH to see if the reduced regeneration rate and the different concentrations effected the amount of alumina dissolved. Since the alumina had been previously filled with Se(VI), the differences in this test of desorption were not considered.

The three columns were dosed equally with 1.5 #/ft^3 NaOH at a flow rate of 1/2 gpm/ft^2, the only difference being the concentrations of NaOH, 2%, 1%, and 0.5%. They were then rinsed with 5 bed volumes of D.I. water. Following this was a 0.05N HCl rinse (6 bed volumes at 1 gpm/ft^2) and subsequent 5 bed volume rinse with D.I. water. The results are listed in Table 18.

TABLE 18

DEGRADATION OF ACTIVATED ALUMINA BY VARIED CONCENTRATIONS OF NaOH AND BY 0.05N HCl ACID RINSE

	Al recovered during Caustic and Subsequent D.I. Rinse (mg) (% by weight of 9-inch column in parentheses)	Al Recovered During 0.05N HCl Rinse and Subsequent D.I. Rinse (mg)
0.5% NaOH	471 (0.86%)	48 (0.09%)
1.0% NaOH	480 (0.87%)	41 (0.07%)
2.0% NaOH	489 (0.89%)	38 (0.07%)

The table shows that the decreased regeneration rate had a large effect on dissolution of alumina when compared with Table 10. The differences noted between the 3 different concentrations of NaOH are not as great as with the previous test, however there is a slight increase in amount dissolved as concentration is increased. The amount of alumina dissolved during the acid rinse increased a little also, from 0.03% with 3 gpm/ft^2 rate to 0.08% with 1 gpm/ft^2.

Based on these results, the following numbers of cycles could be completed at each concentration of NaOH before all of the activated alumina would be dissolved (included in loss due to acid rinse, also):

0.5% NaOH - 106 cycles
1.0% NaOH - 105 cycles
2.0% NaOH - 103 cycles

If this regeneration were done once a day, the media would have to be replaced 3.5 times a year. If it were possible to regenerate less often, then the resultant loss of media would be less.

This information would have to be evaluated more closely in pilot studies. This work indicates that increasing the amount of flow through contact time of NaOH in the bed from 10 minutes (3 gpm/ft^2) to 60 minutes (1/2 gpm/ft^2) will greatly increase the amount of alumina dissolved. The associated replacement costs for this could be very expensive.

SECTION 7
PRELIMINARY COST ESTIMATE

Based on the capacities and regeneration techniques developed during the column studies, separate cost estimates have been prepared for the removal of either Se(IV) or Se(VI) from a ground water similar in chemical composition to the water used during these tests. Main design criteria used to develop the costs include:

Average Flow - 1 mgd
Se(IV) or Se(VI) concentration - 0.10 mg/l
Capacity of Activated Alumina at pH6:

Se(IV)	-	90 mg/l
Se(VI)	-	7 mg/l

Minimum Duration of Treatment Run - 24 hours
Regeneration:
    NaOH - minimum flow through time with 0.5% NaOH of 1.5 hours @ 1 gpm/ft^2
    H_2SO_4 or HCl - same volume of NaOH with a concentration of 0.25% at 2 gpm/ft^2

The system considered would be very basic, with no automatic control systems. Regeneration would be done manually. Capital costs include all manufactured equipment, activated alumina, piping and valves, electrical and instrumentation, a small building for chemical storage and other operations, and contingencies. A small clearwell was provided to supply sufficient regeneration water. Land acquisition is included.

Annual operation and mantenance costs include:

chemicals for regeneration and pH adjustment
labor @ $15,000/yr
media replacement @ 0.5% per regeneration
electrical energy @ 7¢/kw-hr

Current costs used were:

50% NaOH = $175/ton
28% HCl = $65/ton
100% H_2SO_4 = $60/ton
Activated alumina = $0.60/lb

To develop costs on a cents per 1000 gallons produced (¢/1000 gal) or dollars per acre-foot ($/ac-ft.) basis, estimated capital costs were amortized over the life of the equipment, estimated to be 20 years. An annual interest rate was assumed to be 10%. Table 19 lists these estimated costs.

As can be seen, ground water contaminated with only Se(VI) will cost much more to treat than will water with Se(IV) present. If there is an appreciable amount of Se(VI) (>10 ppb) present in a water with Se(IV), then the removal of selenium will be dependent on how well Se(VI) can be removed during treatment.

TABLE 19

COST ESTIMATE FOR Se(IV) OR Se(VI) REMOVAL FACILITIES

	Cost	
Item	Se(IV)	Se(VI)
Amortized Capital Costs ($/yr.)	$27,000	$ 115,000
Operation and Maintenance ($/yr.)	53,000	145,000
Total Annual Costs ($/yr.)	$80,000	$ 260,000

Cost to Treat 100% Se(IV) = 23¢/1000 gal = $75/acre-foot
Cost to Treat 100% Se(VI) = 78¢/1000 gal = $255/acre-foot

Because the reduction of Se(VI) to Se(IV) requires very vigorous reduction, sulfur dioxide or other mild reducing agents could not be used for this purpose. It would be virtually impossible to chemically pretreat a drinking water supply to reduce Se(VI) to Se(IV).

The estimated costs, prepared for this report, are based solely on nine-inch deep columns of alumina. It is quite possible that deeper beds may show a greater capacity for both species of inorganic selenium. To develop truly accurate cost estimates, capacities would have to be developed from pilot scale testing. This testing would also develop other engineering parameters that would allow the rapid determination of the feasibility for using activated alumina to remove selenium from drinking water supplies.

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APPENDIX A
MATERIALS AND INSTRUMENTS

All of the analytical instruments that were used have been described in Chapter 4, except for an Orion pH meter. A list of materials includes:

1. Three Cole-Palmer peristaltic pumps, model #7015.

2. Three variable-speed motors with speed controls, 1/30 hp with an output gear ratio of 12:1 and a maximum speed of 290 rpm, distributed by Minarik Electric Company, Los Angeles.

3. Three automatic samplers, Wastewatcher II, with 24-200 ml conventional polyethylene sample bottles each, manufactured by Raymond Jensen Company, Los Angeles.

4. One six paddle stirrer, manufactured by Phipps and Bird, Inc., Richmond, Virginia.

5. Three 15-inch glass columns of 1-inch inside diameter. Fitted with ground glass joints with ball and socket clamps and stopcocks.

6. Three conventional, nonlinear polyethylene tanks, 55 each.

7. Tygon tubing, 3/16 inch I.D., 3/8 inch O.D.

8. Teflon tubing, 3/16 inch I.D., 1/4 inch O.D.

9. Swagelock fittings, 1/4-inch.

10. Polyethylene sample containers (1- and 4-liter), "Qubetainers" manufactured by Hedwin Corporation, Laporte, Indiana

11. ALCOA activated alumina, type F-1, 14-28, 28-48, and 48-100 mesh.

12. Reagent grade concentrated HCl, H_2SO_4, and HNO_3 and 50 percent NaOH.